CRANFIELD UNIVERSITY

KARINE K. PHILIPPE

# THE ROLE OF ADVANCED OXIDATION PROCESSES IN DRINKING WATER TREATMENT

**SCHOOL OF APPLIED SCIENCES**

Centre for Water Science

**PhD THESIS**

Academic Year: 2009 - 2010

Supervisor: Prof. Simon A. Parsons

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This thesis is submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy

# ABSTRACT

Removal of natural organic matter (NOM) is an ever growing challenge for water utilities as many surface waters used for drinking water in the UK exhibit increasing organics levels and it is well known that these organics can lead to problems such as water colouration, unpleasant odour and taste, bacterial growth and disinfection by-products (DBPs) formation. NOM is traditionally removed by coagulation, however in the case of hydrophilic organic matter rich waters the performances of these processes are not able to remove sufficient organic matter leading to potential failures of DBP regulations. Here two advanced oxidation processes (AOPs) UV/$H_2O_2$ and $TiO_2$ photocatalytic oxidation were studied to investigate how they could be integrated in a drinking water flowsheet to meet this challenge. Substantial structural changes in the organic matter were observed: loss of aromaticity and double bonded character, shift towards lower molecular weight (MW) more hydrophilic compounds and formation of oxygenated by-products. Although hydrophobic rich waters seem more suitable to AOP treatment as preferential attack of high MW hydrophobic compounds was demonstrated, no correlation was found between physical properties of nine NOM surrogates and removal by UV/$TiO_2$. Dark adsorption onto $TiO_2$ was shown to remove preferentially high molecular weight hydrophobic anionic compound such as tannic acid. UV/$H_2O_2$ combined with coagulation did not show any significant benefits in NOM removal as UV/$H_2O_2$ appeared to target similar components as coagulation (high MW, hydrophobic and charged) and to form by-products recalcitrant to coagulation. The combination of both AOPs with fresh GAC showed moderate benefits in

trihalomethane formation potential (THMFP) and non purgeable organic carbon (NPOC) removal highlighting the role of size and surface chemistry on adsorption onto GAC. Biodegradability of the water did not exhibit any significant change after both AOP treatments within the studied conditions possibly due to insufficient UV irradiation and presence of organics recalcitrant to biodegradation.

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# ABBREVIATIONS AND NOTATIONS

α – polarisability

γ – surface tension

ρ – density

·OH – hydroxyl radical

AC – activated carbon

AOM – algal organic matter

AOP – advanced oxidation process

AWWA – American Water Works Association

AwwaRF – American Water Works Association Research Foundation

BAC – biodegradable activated carbon

BDOC – biodegradable organic carbon

BOM – biodegradable organic matter

BV – bed volume

DBP – disinfection by-product

DBPFP – disinfection by-product formation potential

DCAA – dichloroacetic acid

DCAAFP – dichloroacetic acid formation potential

DOC – dissolved organic carbon

DOM – dissolved organic matter

EBCT – empty bed contact time

$E_{bg}$–band gap energy

FAF – fulvic acid fraction

FTIR - Fourier transform infrared spectroscopy

GAC – granular activated carbon

GC-ECD – gas-chromatography electron capture detector

GC-MS – gas-chromatography mass-spectrometry

HAA – haloacetic acid

HAAFP – haloacetic acid formation potential

HAF – humic acid fraction

HP –high pressure

HPI – hydrophilic

HPIA+N – hydrophilic acid and neutral

HPIB – hydrophilic base

HPINA – hydrophilic non-acid

HPO – hydrophobic

HPLC – high performance liquid chromatography

HPON – hydrophobic neutral

HPSEC – high performance size exclusion chromatography

$K_F$ – Freundlich adsorption capacity parameter

LC – large column

log $K_{OC}$ – log (soil-water partition coefficient)

log $K_{OW}$ – log (octanol-water partition coefficient)

LP –low pressure

MCL – maximum concentration limit

MP –medium pressure

MIEX® – magnetic ion exchange

MTBE – methyl tert butyl ether

MW – molecular weight

n – Freundlich adsorption intensity parameter

NOM – natural organic matter

NPOC – non purgeable organic carbon

PAC – powdered activated carbon

POC – particulate organic matter

$pK_a$ – acid dissociation constant

pzc–point of zero charge

polyDADMAC – polydiallyldimethylammonium chloride

PSA – polar surface area

RO – reverse osmosis

RSSCT – rapid small-scale column test

RT– retention time

SC – small column

SHA – slightly hydrophobic acid

Sol – water solubility

SUVA – specific ultraviolet absorbance

TCAA – trichloro acetic acid

THM – trihalomethane

THMFP – trihalomethane formation potential

TOC – total organic carbon

TPI –transphilic acid

UP – ultrapure

USEPA –United States Environmental Protection Agency

UV/$H_2O_2$ – ultraviolet/hydrogen peroxide

UV/$TiO_2$– ultraviolet/titanium dioxide

$UV_{254}$ – ultraviolet (254 nm) absorbance

UV-C – ultraviolet-C irradiation

VHA – very hydrophobic acid

VUV – vacuum ultraviolet

WHO –World Health Organisation

WTW – water treatment works

# 1 Introduction

## 1.1 Background

Water utilities are facing a growing problem throughout the world industry related to the presence of natural organic matter (NOM) in raw waters. A significant body of evidence shows that over the past 20 years a number of rivers and lakes across northern Europe and North America are slowly turning brown as a result of increased levels of organic carbon being released from catchments (Eikebrokk *et al*., 2004; Evans *et al*., 2005). Hypotheses explaining this phenomenon range from climate change to changes in catchment management. Recently, Monteith *et al*. (2007) analysed water quality data from over 500 sites and showed that as acidity in the soil fell the carbon became more soluble, thus moving into lakes and rivers and onto water treatment works (WTWs). The indications from the work of Monteith *et al*. (2007) and others are that these high levels of NOM are stable which imply a significant challenge for the water industry that have historically used many of these waters to supply drinking water to consumers. As NOM can be responsible for water discolouration, unpleasant odour and taste, bacterial growth and disinfection by-products (DBPs) formation increasing organic levels translate into increased costs for treatment and also greater pressures on the use of chlorine based disinfectants (Fabris *et al*., 2008). Chlorine is ubiquitous in water treatment in the UK and worldwide but we are reliant on it to provide safe drinking water.

In the UK only one group of DBPs is currently regulated, the trihalomethanes (THMs) and a maximum concentration value of 100 µg $L^{-1}$ at consumers tap has

been set for the sum of the concentrations of the four THMs (trichloromethane, bromodichloromethane, dibromochloromethane and tribromomethane). The THMs were the first DBPs identified in drinking water (Rook, 1974) but over 600 other DBPs have been reported in the literature (Richardson, 1998). Recent studies have looked at a wider range od DBPs formed in the UK waters including haloacetic acids, haloacetonitriles and nitrosamines (Goslan *et al*., 2009; Bougeard *et al*., 2010). The second most abundant group of DBPs are the haloacetic acids (HAAs). There are nine HAAs in total and whilst there is no current UK regulatory limit for haloacetic acids, the US Environmental Protection Agency (USEPA) have set a maximum concentration limit (MCL) of 60 µg $L^{-1}$ for $HAA_5$ and the World Health Organization (WHO) have suggested that guideline values for monochloro acetic acid (MCAA), dichloro acetic acid (DCAA) and trichloro acetic acid (TCAA) are provisionally established as 20 µg $L^{-1}$, 50 µg $L^{-1}$ and 200 µg $L^{-1}$ respectively. A proposed $HAA_9$ standard of 80 µg $L^{-1}$ is currently under consideration by the European Union (Cortvriend, 2008) and if implemented would cause significant challenges for European and UK water utilities.

NOM is a complex mixture of organic compounds and consists of both hydrophobic and hydrophilic components where the largest fraction is generally hydrophobic acids, which makes up approximately 50% of the dissolved organic carbon (DOC) (Owen *et al*., 1995). These can be described as the aquatic acids or humic substances comprising of humic and fulvic acids. Hydrophilic organics make up the majority of NOM remaining in water after it has passed through conventional or advanced water treatment processes. It can be seen that whilst

all other fractions are removed through treatment the hydrophilic (HPI) fraction is only slightly removed and it makes up the majority of the residual organics in water before chlorination (Leenheer and Croué, 2003).

Whilst obvious issues regarding the reaction of hydrophilic organics with chlorine exist a number of other questions related to the exact composition of this fraction still need an answer. The hydrophilic organic fraction is a heterogeneous mixture of organic molecules characterised by high solubility in water and examples of chemical groups identified in this fraction include alcohols, ketones, esters, alkylhalides and aromatics. Few individual compounds have been identified but any organic compound with a high water solubility (often characterised by a low $K_{ow}$ values), has the potential to be in this fraction.

This project has been supported by Severn Trent Water who are interested in treatment solutions that will allow them to address the need to increase the NOM removal at water treatment works with hydrophilic organic matter rich waters (Figure 1.1). An additional challenge is that these waters have substantial alkalinity levels (> 100 mg $L^{-1}$ as $CaCO_3$). As a result, the conventional approach to remove more NOM using coagulation with metal salts is an expensive process as substantial acid addition is required to reach the optimum treatment conditions (pH 4-5) (Sharp *et al*. 2006). The challenge for drinking water companies is therefore to develop new options allowing a more effective treatment of hydrophilic NOM.

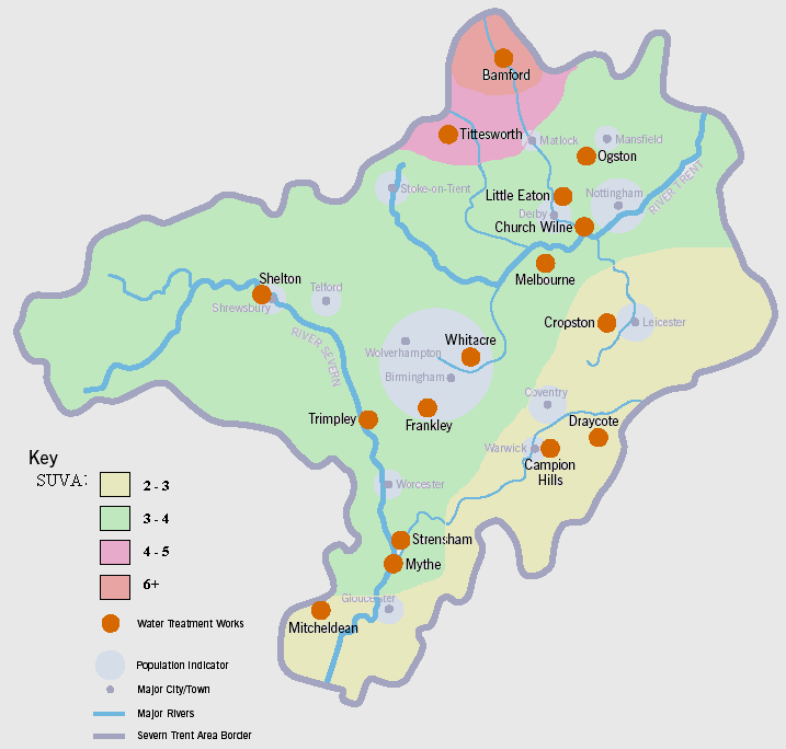


**Figure 1.1 Characterisation of waters in the Severn Trent Water area where Specific UV Absorbance (SUVA) is used to indicate hydrophobicity (Severn Trent Water)**

The literature and previous work at Cranfield University has shown that advanced oxidation processes (AOPs) can be effective at removing NOM. For example, a number of studies highlighted the efficiency of UV/$H_2O_2$ (Backlund, 1992; Wang *et al*., 2000; Kleiser and Frimmel, 2000; Parkinson *et al*., 2001; Thomson *et al*., 2002; Goslan *et al*.,2006; Sarathy and Mohseni, 2007) and of photocatalytic oxidation (Murray and Parsons 2004, Le Clech *et al*., 2006; Liu *et al*. 2008, 2010; Gerrity *et al*., 2009). However to date few studies have investigated the AOP treatment of non humic waters and here we have investigated the use of two AOPs (UV/$H_2O_2$ and photocatalytic oxidation) to treat a hydrophilic rich reservoir water from Severn Trent area. The hypothesis

for this research was that the degradation of NOM molecules by hydroxyl radicals (•OH) generated during the AOP processes would impact on NOM properties such as hydrophobicity, charge and biodegradability that affect removal in downstream processes. Various treatment scenarios have been examined by combining both of the AOPs selected with pre and post coagulation, granular activated carbon (GAC) adsorption and biodegradation processes to evaluate how an AOP could be integrated into a drinking water treatment flowsheet. We are also interested in the link between degradation of NOM structure, treatability and reactivity towards chlorine.

## 1.2 Objectives

As stated above the hypothesis for this project was that the powerful oxidants produced during AOPs would lead to structural changes in NOM compound structure and would therefore increase removal in conventional water treatment processes. Accordingly the main objectives of this thesis were as follows:

1. Assess the performances of UV/$H_2O_2$ and photocatalytic oxidation on NOM removal in the case of a hydrophilic rich raw water.
2. Determine the relationship between NOM characteristics, treatability and DBPs formation using model compounds.
3. Evaluate the potential benefits of coupling UV/$H_2O_2$ or photocatalytic oxidation with a downstream or upstream process such as coagulation, GAC or biotreatment in the case of a hydrophilic rich raw water.

## 1.3 Thesis structure

This thesis takes the form of a series of chapters formatted as papers for publication. All papers were written by the first author, Karine Philippe and have been edited by Prof. Simon Parsons, Dr Bruce Jefferson and Dr Jitka Macadam. All the experimental work was undertaken by Karine Philippe with the following exceptions. Chapter 3: GAC isotherms tests on UV/$H_2O_2$ treated water performed by Alba Anfruns, visiting PhD student. Alba also supported the setting up the rapid small scale column test (RSSCT) rig. Chapter 4 and 5: THM formation potential (THMFP) analysis was conducted by Claudia Hans as part of her internship.

Chapter 2 is a review of investigations related to UV/$H_2O_2$ and photocatalytic oxidation applied to NOM removal. It also summarises the main findings on AOPs (including ozonation) combined with coagulation, fresh GAC or biotreatment as downstream processes: The *advanced oxidation processes in drinking water treatment.* The aim of this chapter is to identify the main parameters affecting the performances of both AOPs and determine the link between chemical and physical properties of NOM and treatability. The effects on the NOM structure and oxidation by-products formation are also examined.

The UV/$H_2O_2$ treatment of a high alkalinity hydrophilic rich raw water is studied in Chapter 3 *UV/$H_2O_2$ treatment of an hydrophilic natural organic matter rich reservoir water and its combination with coagulation, GAC adsorption and*

*biodegradation processes* by K.K.Philippe, A.Anfruns, M.J.Martin, M.A.Montes-Morán, J.MacAdam, J.Hart, B.Jefferson, S.A.Parsons is being prepared for submission. The chapter highlights the treatment performances on NOM and THM precursor removal as well as the impact of UV/$H_2O_2$ on NOM structure. The coupling of UV/$H_2O_2$ with coagulation, GAC and biotreatment is then investigated.

Chapter 4 entitled *Photocatalytic oxidation, GAC and biotreatment combination: an alternative to coagulation of hydrophilic rich waters?* by K.K.Philippe, C.Hans, J.Macadam, B.Jefferson, J.Hart, S.A.Parsons is currently in press in the journal *Environmental Technology*. This chapter describes the impact of photocatalytic oxidation on NOM removal and THM formation in the case of a high alkalinity hydrophilic rich water. Combination with downstream processes (fresh GAC and biotreatment) is also reported.

Chapter 5 entitled *Photocatalytic oxidation of NOM surrogates and impact on THM precursor formation* by K.K.Philippe, C.Hans, J.Macadam, B.Jefferson, J.Hart, S.A.Parsons has been submitted to the journal *Chemosphere*. It examines the photocatalytic oxidation of nine model compounds representative of NOM (five amino acids, two carbohydrates and two phenolic compounds) comparing removal and THM formation. The objective is to link chemical and physical properties of organics to treatability and reactivity to chlorine. Both dark adsorption onto $TiO_2$ and photocatalytic oxidation are considered in the study.

The combined findings of all the papers are discussed within Chapter 6 highlighting the theoretical and practical implications for water treatment. Finally

Chapter 7 summarises the key findings of the study and recommendations for future work to extend the knowledge on NOM treatment by AOPs.

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# 2 The advanced oxidation processes in drinking water treatment

## 2.1 Introduction

### 2.1.1 The natural organic matter (NOM) in drinking water treatment

#### *2.1.1.1 Definition and problems caused by NOM*

Many countries in North America and Northern Europe have indicated an increase in NOM concentration in water sources due to issues with global warming, drought severity and intensive rain events (Fabris *et al*., 2008). NOM describes a complex matrix of humic material from terrestrial origin or allochthonous, and of non humic material from biological origin or autochthonous (Krasner et al. 1996c), which is present in all ground and surface waters. NOM consists of dissolved organic matter (DOM) and particulate organic matter (POM) and its composition can vary both spatially and temporally (Goslan *et al*. 2002; Sharp *et al*., 2006). Size can range in molecular weight (MW) from a few hundred to 100,000 Daltons (Da), which is in the colloidal size range. The NOM composition can be described as a complex mixture of aromatic and aliphatic hydrocarbon structures with various functional groups such as amide, carboxyl, hydroxyl and ketone (Leenheer and Croué, 2003).

NOM can cause aesthetic concerns such as colouration, unpleasant taste and odour of the water. It can also act as a substrate to bacterial growth (Fabris *et al*., 2008). Last but not least, natural organic matter (NOM) is the main

precursor of disinfection by-products (DBPs) in potable water which are of health concern (Bougeard *et al*., 2010).

Traditionally, conventional coagulation/flocculation using inorganic coagulants is the main drinking water treatment process. The NOM characteristics play a key role to choose the adequate treatment option. Hydrophobic NOM has been shown to be more readily removed by conventional coagulation than hydrophilic NOM (Sharp *et al*., 2006; Bond *et al*., 2010). Alternative processes have been developed to enhance the organics removal such as adsorption on activated carbon (Summers and Roberts, 1998), ion exchange (Bolto et al., 2004), MIEX (Mergen et al., 2008), membrane filtration (Lee et al., 2007), ozonation (Graham, 1999).

*2.1.1.2 Characterisation methods*

Leenheer and Croué (2003) have discussed the various techniques used to characterise NOM. NOM investigations can be divided in two categories: whole water studies and studies on fractions where NOM is isolated from the water matrix. Since NOM composition is complex to define, bulk parameters are commonly used to characterise NOM. Total organic carbon (TOC) is the most comprehensive measurement to quantify NOM. TOC is composed of dissolved organic carbon (DOC) which is ≤ 0.45 µm and particulate organic carbon (POC) which is ≥0.45 µm. POC represents generally less than 10% of TOC. DOC concentrations range from 0.1 mg $L^{-1}$ in groundwater to 50 mg $L^{-1}$ in bogs. Although the majority of NOM is refractory to rapid biodegradation, the existence of biodegradable organic matter (BOM) should be mentioned. BOM is

usually measured as biodegradable organic carbon (BDOC) and BDOC concentration in water depend on the origin of NOM as autochthonous (algal and bacterial origin) is more biodegradable than allochthonous NOM (terrestrial origin).

Fractionation of NOM using resin sorbents is a useful technique to characterise NOM. Fractionation procedures involving one, two or three different resin sorbents of different polarity and enable to isolate humic/hydrophobic material and non humic/hydrophilic material. Spectrophotometric measurements such as ultraviolet (UV) absorbance (mostly at 254 nm) and fluorescence measurements can be a complement to DOC measurements since aromatic compounds (mostly humic) present in surface waters are both chromophores and fluorophores. Specific UV absorbance (SUVA) defined as the ratio of UV absorbance at 254 nm by DOC can help to characterise the hydrophobicity of a water. SUVA ≤ 2 L $m^{-1}$ $mg^{-1}$ refers to hydrophilic rich water while high SUVA waters (≥4) refers to hydrophobic rich waters. NOM can also be characterised by size. A common method is high performance size exclusion chromatography (HPSEC) coupled with a UV detector. In this method, large sized molecules are eluted first while small sized molecules which have a stronger affinity with the column have longer retention times. Average molecular weight is usually in Daltons. Pyrolysis gas chromatography-mass spectroscopy (GC-MS) is another analytical technique which degrades natural biopolymers into their low MW decomposition products following a heating process at high temperature. This allows a clear identification of the biopolymers composing the bulk NOM based on the specific fragmentation pathway of each biopolymer. On the other hand,

Leenheer and Croué (2003) described a preparative fractionation method as a comprehensive approach to characterise NOM. The authors provide a classification based on size and polarity, acid/ neutral/basic character and compounds classes (fulvic acid, hydrocarbons, aromatics, sugars, aminoacids...).

### 2.1.2 Fundamentals of UV photolysis

UV photolysis has been described in detail by Stefan (2004). Light has both wave and particle properties. Light is an electromagnetic radiation where its wavelength λ (nm) is defined as the ratio of the velocity of light *c* (in vacuum. *c* is equal to $3.0 \times 10^{8}$ m $s^{-1}$) by its radiation frequency *v* ($s^{-1}$). Light is absorbed or emitted in discrete units of energy *E*, called *quanta* (*hv*) where the Planck's constant. *h* is equal to $6.6256 \times 10^{-34}$ J s.

The main UV spectral range for UV photolysis in water applications is UVC (200-280 nm) and this is where both water constituents such as dissolved organic and inorganic compounds absorb radiation but also a number of important pollutants such as pesticides and taste and odour compounds (Table 2.1).

**Table 2.1 Light electromagnetic spectrum characteristics**

| Radiation name | Wavelength range (nm) | Energy (kJ $mol^{-1}$) |
|---|---|---|
| Near IR (InfraRed) | 700-1000 | 120-171 |
| Visible | 400-700 | 171-299 |
| UVA | 315-400 | 299-380 |
| UVB | 280-315 | 380-427 |
| UVC | 200-280 | 427-598 |
| VUV (Vacuum UV) | 100-200 | 598-1196 |

The two most used UV sources are the low pressure (LP) mercury (Hg) vapour lamp and the medium pressure (MP) mercury vapour lamp. LP UV lamps are characterised by a single UV output at 253.7 nm wavelength whereas MP UV lamps spectrum is polychromatic (200-400 nm).

The other UV range of interest in water treatment is the vacuum UV (VUV) range (100-200 nm) as this radiation is absorbed by water, generating highly reactive species such as hydroxyl radicals that further induce oxidative degradation.

$$H_2O + h\nu\ (\lambda < 190\ nm) \rightarrow H^{\bullet} + {}^{\bullet}OH \qquad (2.1)$$

We are interested here in using UV to transform and oxidise organic matter. First we must consider the first law of photochemistry which states that only the light that is absorbed by a molecule can be effective in producing a

photochemical change in that molecule. The absorption spectrum characteristics depend on the molecular structure of the absorber and on the interactions between that compound and the solvent. Most UV light absorbers contain double bonds or conjugated double bonds, involving carbon, nitrogen or oxygen atoms, and are characterised by delocalised π-electrons. Such systems are called chromophores. The environmental pollutants containing chromophoric structures include alkenes, aromatic and heterocyclic compounds, aldehydes, ketones and carboxylic acids (Ikehata *et al*, 2006).

### 2.1.3 The advanced oxidation processes (AOPs)

Advanced oxidation processes (AOPs) are a range of chemical oxidation processes that have been proposed for water treatment for over 40 years (Parsons and Williams, 2004). These processes are primarily based on the formation of a highly reactive hydroxyl radicals (•OH) (oxidation potential of 2.8 V) which are the most oxidative species after fluorine (oxidation potential of 3.03 V). •OH have been shown to be capable of degrading a whole range of organic and inorganic pollutants with rate constant in the range of $10^8$ to $10^{10}$ $M^{-1}$ $s^{-1}$ faster than ozone (~10 $M^{-1}$ $s^{-1}$) (Legrini *et al*., 1993). •OH is a free radical where the symbol • represent a single unpaired electron. Once a free radical has been initiated by photolysis, hydrogen peroxide, ozone etc. then numerous simple radical reactions can occur. This explains the complex chemistry of such systems as mechanisms are difficult to predict as well as the identity of all oxidation by-products. A number of AOPs are commercially available. For

example, UV is used as a disinfection process in more than 3000 plants in Europe and in the USA. Other applications involve the combination with chemicals such as $H_2O_2$, $O_3$, and Fenton's reagent (Fe as a catalyst with $H_2O_2$ solution).

In this thesis we have studied two of the most popular AOPs namely UV/$H_2O_2$ and UV/$TiO_2$. UV/$H_2O_2$ is the most widely applied AOP and in principle is relatively simple where $H_2O_2$ molecules are irradiated with UV light and form •OH radicals. The second process is described as photocatalytic oxidation and here $TiO_2$ a semi conductor is UV-irradiated forming oxidative holes, •OH radicals and superoxide radicals $•O_2^-$. Due to oxygen vacancies, $TiO_2$ is an n-type semiconductor and has the ability to undergo photoinduced electron transfer to an adsorbed particle. The mechanistics aspects and various applications of photocatalytic oxidation have been reported elsewhere (Hoffmann *et al*., 1995; Fujishima *et al*., 2000; Augugliaro *et al*., 2009). In this review, we have focussed on the performances of these two different processes as well as UV direct photolysis for the removal and transformation of natural organic matter (in terms of DOC, $UV_{254}$ and DBP formation potential) and have where possible identified the key parameters affecting the process efficiency and their application in potable water treatment. The benefits of combining these two AOPs with other water treatment processes including coagulation, adsorption (GAC) and biotreatment are also discussed.

### *2.1.3.1 Fundamentals of UV/$H_2O_2$*

In the UV/$H_2O_2$ process, hydrogen peroxide is cleaved into two hydroxyl radicals by UV photolysis at 253.7 nm. This process has a quantum yield of 0.98 (Legrini *et al*., 1993) which means that 2 moles of hydroxyl radicals are formed per mole of photons absorbed.

$$HO : OH + hv\ (\lambda < 568\ nm) \rightarrow HO^{\bullet} + {}^{\bullet}OH \qquad (2.2)$$

Hydroxyl radicals are extremely reactive, short lived (≈10 μs) species that can undertake a wide variety of reactions with organic molecules in water. Whilst often reported as being unselective $HO^{\bullet}$ react preferentially with electron rich aromatic and olefin moieties over saturated carbon structures (Tuhkanen, 2004). Reactions of hydroxyl radicals generated in the presence of an organic substrate may be differentiated by their mechanisms into three different classes:

- Hydrogen abstraction

$$HO^{\bullet} + RH \rightarrow R^{\bullet} + H_2O \qquad (2.3)$$

- Electrophilic addition

$$HO^{\bullet} + PhX \rightarrow HOPhX^{\bullet} \qquad (2.4)$$

Where Ph is an aromatic system and X is a halogen.

- Electron transfer

$$HO^{\bullet} + RX \rightarrow RX^{\bullet+} + OH^{-} \qquad (2.5)$$

Radical-radical recombination should also be taken into account:

$$2\ HO^{\bullet} \rightarrow H_2O_2 \qquad (2.6)$$

### *2.1.3.2 Fundamentals of $TiO_2$-photocatalysed oxidation*

In semiconductor photocatalysis, the light absorbing species is a semiconducting material. A semiconductor is characterised by its valance band (VB) and its conductance band (CB). VB is by definition the highest occupied band full of electrons whereas CB is the lowest unoccupied band. The energy difference between CB and VB is called the band gap energy $E_{bg}$. The overall reaction between an electron donor D adsorbed on the surface of the semiconductor particles and an electron acceptor A from the surface is as follows:

$$A + D + h\gamma \rightarrow A^- + D^+ \qquad (2.7)$$

Where $h\gamma \geq E_{bg}$

A has accepted a photogenerated electron $e^-$ from CB to generate a reduced $A^-$ while D has reacted with a photogenerated hole $h^+$ to generate an oxidised product $D^+$.

In the application of water purification, A is the dissolved oxygen and D is the pollutant, in our case the NOM.

$$NOM + O_2 + h\gamma \rightarrow CO_2 + H_2O + \text{minerals} \qquad (2.8)$$

Where $h\gamma \geq E_{bg}$

The semiconductor should be photocatalytically active, sensitive to visible or UV light, biologically and chemically inert, inexpensive and photostable. Titanium dioxide $TiO_2$ is a good candidate with $E_{bg}$ of 3-3.2 eV absorbing UV light (<380nm). The crystalline form commonly used is anatase as it is the easiest to produce and the most photocatalytically active.

($>Ti^{IV}OH$) are surface hydroxyl groups which are oxidised on $TiO_2$ surface to hydroxyl radicals ($>Ti^{IV}OH^{\bullet+}$) which then oxidise the pollutant. The primary processes involved in the $TiO_2$ sensitised photomineralisation of organic pollutants are as follows (Hoffmann *et al*, 1995):

-Charge-carrier generation

$$TiO_2 + h\gamma \rightarrow h^+ + e^- \quad (2.9)$$

-Charge-carrier trapping

$$h^+ + \geq Ti^{IV}OH \rightarrow (\geq Ti^{IV}OH^{\bullet+}) \quad (2.10)$$

$$e^- + \geq Ti^{IV}OH \leftrightarrow (\geq Ti^{III}OH) \quad (2.11)$$

$$e^- + \geq Ti^{IV} \rightarrow Ti^{III} \quad (2.12)$$

-Charge-carrier recombination

$$e^- + (\geq Ti^{IV}OH^{\bullet+}) \rightarrow \geq Ti^{IV}OH \quad (2.13)$$

$$h^+ + \geq Ti^{III}OH \rightarrow Ti^{IV}OH \quad (2.14)$$

-Interfacial charge transfer

$(\geq Ti^{IV}OH^{\bullet+})$ + organic pollutant → $\geq Ti^{IV}OH$ + oxidised pollutant (2.15)

$(\geq Ti^{III}OH) + O_2 \rightarrow \geq Ti^{IV}OH + O_2^{\bullet-}$ (2.16)

## 2.2 NOM removal by UV and UV/$H_2O_2$ treatment

### 2.2.1 Bulk parameters

A number of papers have reported NOM and model compounds such as humic acid degradation by UV and the UV/$H_2O_2$ based advanced oxidation process using different irradiation devices at varying UV lamp wavelengths, varying reactor dimensions and a very wide range of $H_2O_2$ doses (3.4-1000 mg $L^{-1}$) (Table 2.2). Performances were sometimes difficult to compare as UV systems differed by their design and the calibration in J $cm^{-2}$ was not always mentioned.

UV direct photolysis has shown to be efficient at degrading NOM but only at high UV doses which are not likely to be cost effective. For example, Parkinson *et al*. (2001) reported 75% and 100% as DOC and $UV_{254}$ removals respectively after 2400 min UVC irradiation (15 W-low pressure lamp; 0.5 L). Similar results were reported by Thomson *et al*. (2002b) and Buchanan *et al*. (2004) highlighting the fact that mineralisation was more difficult to achieve that degradation of aromatics and double bonded systems. NOM exhibiting a higher aromaticity (as $UV_{254}$ value) usually had a higher removal. It is known that adding $H_2O_2$ (14-50 mg $L^{-1}$) increased significantly the performances of the process (Parkinson *et al*. 2001; Thomson *et al*., 2004b).

A number of studies reported significant DOC, $UV_{254}$ and DBPs removal after $UV/H_2O_2$ treatment. As expected the removal of NOM has been shown to be dependent on the type of organics but also the treatment conditions. For example many studies have investigated waters rich in humic acids-type material and typically exhibited substantial NOM removals. For example, Backlund (1992) studied the $UV/H_2O_2$ degradation of natural humic water (DOC=17 mg $L^{-1}$) from Lake Savojarvi, Finland using nine low pressure UV lamps (15 W; 0.5 L) emitting at 253.7 nm in series and 90 mg/L as $H_2O_2$ dose. After 30 min irradiation, 96% and 77% as $UV_{254}$ and DOC removals were achieved respectively. Wang *et al*. (2000) also reported substantial DOC removal of 5 mg $L^{-1}$ of humic acid using a 8 L batch photoreactor equipped with a high pressure UV lamp of 450 W and 0.86 mg $L^{-1}$ of $H_2O_2$. Goslan *et al*. (2006) investigated the $UV/H_2O_2$ treatment of a high DOC reservoir water (17.4 mg $L^{-1}$) in a collimated beam device (0.5 L) which consisted of four 12 W low pressure mercury UV lamps and treatment resulted in 90% and 80% as $UV_{254}$ and DOC removals respectively at 20 J $cm^{-2}$ and 102 mg $L^{-1}$ of $H_2O_2$.

Two Australian raw waters of specific UV absorbance (SUVA) 1.9 and 3.7 L $mg^{-1}$ $m^{-1}$ exhibited 75-88% DOC removals and almost complete $UV_{254}$ removals after 150 min UV-C irradiation (15 W-low pressure lamp; 0.5 L) and 50 mg $L^{-1}$ of $H_2O_2$ (Parkinson *et al*., 2001). Here, good removals were obtained in spite of the different NOM characteristics as SUVA < 2 corresponds to mostly non humic, low hydrophobicity waters while SUVA > 4 is related to mostly humic, high hydrophobicity waters (Edzwald and Tobiason, 1999).

Lower UV doses (up to 2 J $cm^{-2}$) and 20 mg $L^{-1}$ of $H_2O_2$ were applied to treat low DOC raw waters (2 mg $L^{-1}$) in a collimated beam device (0.2-0.9 L) (Toor and Mohseni, 2007; Sarathy and Mohseni, 2009). Poor DOC removal (15%) was reported while maximum $UV_{254}$ did not exceed 50%.

### 2.2.2 Parameters affecting process efficiency

UV dose (0-1 J $L^{-1}$) and $H_2O_2$ dose (2-52 mg $L^{-1}$) have been shown to be directly correlated to the •OH radical exposure (0-50 x $10^{13}$ M min) (Rosenfeldt *et al*., 2006). The authors highlighted that medium pressure (MP) UV lamp systems were consistently less efficient for •OH radical production than low pressure (LP) UV lamp systems. This was attributed to the relative inefficiency associated with UV output of MP lamps and UV light absorption by $H_2O_2$.

It is also known that the presence of hydroxyl radical scavengers could affect the AOP performances. For example, an excess of $H_2O_2$ (1 g $L^{-1}$) has been shown to have a detrimental effect on the NOM degradation (Backlund, 1992) according to the following reaction:

$$^{\bullet}OH + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \qquad (2.17)$$

This was further confirmed by Wang *et al*. (2001) who tested initial $H_2O_2$ concentrations from 4 to 10 mg $L^{-1}$. The authors also reported that the presence of carbonate species $HCO_3^-/CO_3^{2-}$ (up to 0.04 mg $L^{-1}$) reduced the process efficiency due to scavenging of hydroxyl radicals according to the following reactions:

$$^{\bullet}OH + HCO_3^- \rightarrow OH^- + HCO_3^{\bullet} \quad (2.18)$$

$$^{\bullet}OH + CO_3^{2-} \rightarrow OH^- + CO_3^{-\bullet} \quad (2.19)$$

NOM itself can be seen as a hydroxyl radical scavenger since a fraction of the UV light photolyses directly humic material while the other fraction reacts with $H_2O_2$ (Liao and Gurol, 1995). The authors also highlighted that pH (over a range 2-10) affected significantly the UV/$H_2O_2$ process as pH ≥ 5 resulted in a reduction in oxidation efficiency. At this pH, the equilibrium shifted towards the bicarbonate ion, which was expected to scavenge hydroxyl radicals. At pH 7, bicarbonate ions were transformed into carbonate ions which have an even higher reactivity towards hydroxyl radicals thus enhancing the scavenging effect. However, in presence of chloride ions, neutral or alkaline conditions were beneficial to UV/$H_2O_2$ (Liao *et al*., 2001). It was suggested that hydroxyl radicals were scavenged by the chloride as:

$$HO\bullet + Cl^- \rightarrow HOCl^-\bullet \quad (2.20)$$

The $HOCl^-\bullet$ could then dissociate back to chloride and hydroxyl radicals. The other possibility would be that $HOCl^-\bullet$ was converted to chlorine atom through the following protonation reaction:

$$HOCl^-\bullet + H^+ \rightarrow Cl\bullet + H_2O \quad (2.21)$$

### 2.2.3 UV/$H_2O_2$ impact on NOM characteristics

#### *2.2.3.1 Molecular weight (MW) distribution*

Although complete mineralisation of NOM by UV/$H_2O_2$ was not reported, a number of studies highlighted the significant impact of the process on the MW distribution using HPSEC analysis. For example, Thomson *et al*. (2002b) demonstrated the preferential removal of larger molecules after UV-C irradiation (39 W) of a natural raw water at 30 to 300 min retention time and 11 mg $L^{-1}$ $H_2O_2$. In another study (2004b), the authors demonstrated that hydroxyl radicals reacted specifically with intermediate size compounds while ozone attack was non size specific. It should be noted that no MW values were indicated on the HPSEC chromatograms but only retention times. Wang *et al*. (2006) demonstrated that intermediate by-products < 10 KDa were formed when irradiation time was < 30 min (450 W, high pressure UV lamp) and then further degraded after 30 min. Similarly, Sarathy and Mohseni (2007) described a shift towards smaller MW compounds after UV/$H_2O_2$ treatment of a raw reservoir water up to 1.5 J $cm^{-2}$ and 20 mg $L^{-1}$ of $H_2O_2$. These results suggest that hydroxyl radicals preferentially reacted with high molecular weight species (>1200 Da) leading to the formation of low MW species (<750 Da). So whilst hydroxyl radicals are non-specific reactive species, here the reaction rate constant between the hydroxyl radicals and NOM seemed to be dependent on the MW of the NOM. This agrees with Westerhoff *et al*. (1999) who highlighted a positive correlation between MW and aromaticity of NOM and the reaction rate constant between the hydroxyl radicals and the NOM. Conversely,

Espinoza and Frimmel (2009) found no evidence of hydroxyl radical selectivity for UV/$H_2O_2$ systems using a simple physical model.

*2.2.3.2 Hydrophobicity*

Sarathy and Mohseni (2009) reported the effect of UV/$H_2O_2$ on the hydrophobicity of the NOM of a low DOC (2 mg $L^{-1}$) reservoir water. The fractionation method was not sensitive to detect small DOC changes but the ratio of hydrophilic NOM by hydrophobic NOM indicated that the treatment reacted preferentially with hydrophobic material leading to the formation of hydrophilic by-products. At 1.5 J $cm^{-2}$ and 20 mg $L^{-1}$ of $H_2O_2$, 25% of hydrophobic NOM was converted into hydrophilic NOM. Buchanan *et al*. (2005) fractionated a UV treated water (0-233 J $cm^{-2}$) into four fractions. The very hydrophobic acid fraction was found to be highly prone to oxidation while the hydrophilic neutral fraction was the most recalcitrant to UV direct photolysis. According to the authors, the high MW compounds from the very hydrophobic acid fraction and slightly hydrophobic acid fraction were fragmented and contributed to hydrophilic charged and hydrophilic neutral fractions to form biodegradable, low MW, non UV absorbing by-products.

## 2.2.4 UV/$H_2O_2$ by-products

A number of degradation by-products after UV/$H_2O_2$ have been reported in the literature. These are mainly low MW oxygenated compounds such as aldehydes, ketones and carboxylic acids. For example, Backlund (1992)

demonstrated the formation of oxalic, acetic, malonic and n-butanoic acids accounting for 80% of the total DOC after UV/ $H_2O_2$ treatment of a raw lake water. Formaldehyde (4.2-35.5 µM) and acetaldehyde (0.3-36.2 µM) were found to be the main carbonyl low MW by-products detected by Thomson *et al*. (2004b) after an irradiation time of 10 to 180 min (39 W) and 14 mg $L^{-1}$ of $H_2O_2$. Others by-products included propanal (0.1 µM), glyoxal (0.5-2.4 µM), methyl glyoxal (0.2-2.8 µM), glyoxylic acid (0.4-1.1 µM). Similarly, Sarathy and Mohseni (2009) detected an increase in the concentration of four aldehydes: formaldehyde (25-75 µg $L^{-1}$), acetaldehyde (~10-50 µg $L^{-1}$), butanal (< 25 µg $L^{-1}$) and propanal (< 10 µg $L^{-1}$) using increasing UV doses (0.34-1.35 J $cm^{-2}$) and $H_2O_2$ doses (0-20 mg $L^{-1}$). This is consistent with the enhancement in hydrophilic character and biodegradability reported by the authors. Similarly Brinkmann *et al*. (2003) described the effects of simulated solar UV light (6-150 W $m^{-2}$ at 292-500 nm) on a bog lake water (DOC=20.6 mg $L^{-1}$ and $UV_{254}$=111 $m^{-1}$) and reported the formation of low MW organic acids such as formic, acetic, pyruvic, oxalic, malonic and succinic acids. They contributed from 0.31% of the raw water DOC to 6.4% of the DOC after 24 h irradiation and 33% of the bioavailable photoproducts of NOM were comprised of these low MW organic acids.

Concerning THM and HAA precursors, substantial removals have been reported after UV/$H_2O_2$ treatment of natural and modelled waters. For example, UV/$H_2O_2$ treatment of humic acid resulted in 80% trihalomethane formation potential (THMFP) removal after 30 min UV irradiation (450 W high pressure lamp) and 1100 mg $L^{-1}$ of $H_2O_2$ (Wang *et al*., 2006). However, UV dose seems

to be key parameter in the DBP formation as Kleiser and Frimmel (2000) observed an increase of 20% in THMFP after 100 min UV irradiation (15 W) in presence of 8 mg $L^{-1}$ $H_2O_2$ while a 20% reduction was observed after 1000 min. Similarly, THMFP increase was indicated by Thomson *et al*. (2004b) for small and intermediate UV dose (~6 J $cm^{-2}$) while THMFP decreased for large UV doses (~230 J $cm^{-2}$) in presence of 14 mg $L^{-1}$ $H_2O_2$. The authors also demonstrated that THM speciation was dependent on DOC concentration, with more highly brominated compounds detected for lower DOC samples. Toor and Mohseni (2007) investigated the fate of THM and HAA precursors during UV/$H_2O_2$ treatment (0-3.5 J $cm^{-2}$; 0-23 mg $L^{-1}$ $H_2O_2$) of a low DOC (2 mg $L^{-1}$) reservoir water. The authors reported no significant effect of UV direct photolysis on THMFP at the doses tested while UV/$H_2O_2$ resulted in THMFP decrease only at UV doses > 1 J $cm^{-2}$ and $H_2O_2$ doses > 23 mg $L^{-1}$. No significant change was observed below those doses. UV/$H_2O_2$ was found to increase dichloroacetic acid formation potential (DCAAFP) at all doses tested while trichloroacetic acid formation potential (TCAAFP) was following the same trend as THMFP. Bond *et al*. (2009a) also indicated HAAFP increase up to 80 µg $mgDOC^{-1}$ after UVC irradiation (0-180 J $cm^{-2}$) of nine NOM surrogates whilst substantial increase of ~40 µg $mgDOC^{-1}$ was observed for two hydrophilic compounds ($_L$-glutamic acid and $_L$-leucine) treated by UV/$H_2O_2$(0-80 J $cm^{-2}$; 68 mg $L^{-1}$ $H_2O_2$ ).

If the health risks caused by DBPs are well known, the potential toxicity of other UV/$H_2O_2$ by-products has not been widely assessed. Backlund (1992) reported no significant change in mutagenic activity after UV and UV/$H_2O_2$ treatment of a

natural humic water. Parkinson *et al*. (2001) performed acute immobilisation, cytotoxicity and Microtox$^{TM}$ tests using UVC and UV/$H_2O_2$ treated water samples. Acute toxicity was reported after UVC and UV/$H_2O_2$ treatment which was attributed to the release of free copper ions in photooxidised waters. However, these were below regulated levels. Buchanan et al. (2006) highlighted that UV (23-138 J $cm^{-2}$) and VUV (16-160 J $cm^{-2}$) processes produced nitrite $NO_2^-$ (up to 0.23 µg $L^{-1}$) and $H_2O_2$ (up to 1.5 mg $L^{-1}$) that were successfully removed by biotreatment. Irradiated samples were deemed non-cytotoxic and non-mutagenic.

**Table 2.2 Review of experimental conditions and results of UV/$H_2O_2$ process on NOM**

| Water quality | Light | Volume (L) | $H_2O_2$ (mg/L) | T (ºC) | pH | Time (min) | DOC removal | $UV_{254}$ removal | Parameters | Reference |
|---|---|---|---|---|---|---|---|---|---|---|
| Raw lake water, DOC= 17 mg $L^{-1}$, $UV_{254}$= 80 $m^{-1}$ SUVA= 4.7 L $mg^{-1}$ $m^{-1}$ | LP, 135 W at 253.7 nm | 0.5<br>1 | 90 | | 5.6 | 30 | 77% | 96% | DOC, UVabs, molecular size distribution, pH, mutagenic activity, organic degradation products | Backlund, 1992 |
| Humic acid, DOC=5 mg $L^{-1}$ | HP, 450 W at 200-450nm | 8 | 0.86 | 25 | 7 | 60 | 90% | | UV sources, $H_2O_2$ concentration, humic acid concentration, carbonate species content | Wang et al., 2000 |
| Raw river water, DOC= 2.03 mg $L^{-1}$, $UV_{254}$=4.2 $m^{-1}$, SUVA= 2.1 L $mg^{-1}$ $m^{-1}$, 2.5 mg $L^{-1}$ as $CaCO_3$ | LP, 15 W | 1.4 | 16 | 20 | 7.6 | 250 | 10% | 60% | DOC, UVabs, $H_2O_2$ concentration, THMFP | Kleiser and Frimmel, 2000 |

| **Water quality** | **Light** | **Volume (L)** | **$H_2O_2$ (mg/L)** | **T (ºC)** | **pH** | **Time (min)** | **DOC removal** | **$UV_{254}$ removal** | **Parameters** | **Reference** |
|---|---|---|---|---|---|---|---|---|---|---|
| Humic acid, DOC= 3-5 mg $L^{-1}$ | HP, 450 W at 200-700nm | 8 | 4.3 | 25 | 7 | 180 | 80% | | DOC, residual $H_2O_2$, aeration condition, carbonate species content | Wang et al., 2001 |
| MIEX concentrate Hope Valley, DOC= 8.54 mg $L^{-1}$, $UV_{254}$=32 $m^{-1}$, SUVA= 3.7 L $mg^{-1}$ $m^{-1}$, 2.5 mg $L^{-1}$ as $CaCO_3$ | LP, 15 W, 2.34 mW/$cm^2$ | 0.5 | 0<br>50 | 25 | 7.08 | 2400<br>150 | 75%<br>88% | 100%<br>100% | DOC, UVabs, UV sources, toxicity | Parkinson et al., 2001 |
| Raw water Hope Valley, DOC= 6.15 mg $L^{-}1$, $UV_{254}$=11 $m^{-1}$, SUVA= 1.9 L $mg^{-1}$ $m^{-1}$, 89.9 mg $L^{-1}$ as $CaCO_3$ | LP, 15 W, 2.34 mW/$cm^2$ | 0.5 | 0<br>50 | | 7.9 | 2400<br>150 | 40%<br>75% | 100%<br>98% | DOC, UVabs, UV sources, toxicity | Parkinson et al., 2001 |

| **Water quality** | **Light** | **Volume (L)** | **$H_2O_2$ (mg/L)** | **T (ºC)** | **pH** | **Time (min)** | **DOC removal** | **$UV_{254}$ removal** | **Parameters** | **Reference** |
|---|---|---|---|---|---|---|---|---|---|---|
| Raw water , Horsham, DOC= 10.2 mg $L^{-1}$, $UV_{254}$=32 $m^{-1}$, SUVA= 3.1 L $mg^{-1}$ $m^{-1}$, 21.9 mg $L^{-1}$ as $CaCO_3$ | LP, 15 W, 2.34 mW $cm^{-2}$ | 0.5 | 0 | | 7.2 | 2400 | 100% | 65% | DOC, UVabs, UV sources, toxicity | Parkinson et al., 2001 |
| Raw water, Victoria, DOC= 9.7 mg $L^{-1}$, $UV_{254}$=16 $m^{-1}$, SUVA= 1.7 L $mg^{-1}$ $m^{-1}$, 31 mg $L^{-1}$ as $CaCO_3$ | Two LP lamps, 0.81 W per lamp, 26 J $cm^{--2}$ | | 0 | 25 | 7.7 | 240 | 16% | 50% | DOC, UVabs, biodegradability, molecular size distribution, chlorine demand, low MW carbonyl compounds | Thomson et al., 2002a |
| Raw water, Victoria, DOC= 11.4 mg $L^{-1}$, $UV_{254}$= 46 $m^{-1}$, SUVA= 4.1 L $mg^{-1}$ $m^{-1}$ | LP, 39 W at 254 nm | 0.9 | 10.5 | 23 | 7.7 | 90 | 40% | 70% | DOC, UVabs, molecular size distribution, $H_2O_2$ concentration, $E_{E0}$ | Thomson et al., 2002b |
| | | | 24 | | | 90 | 70% | 85% | | |
| | | | 58 | | | 60 | 90% | 85% | | |

| **Water quality** | **Light** | **Volume (L)** | **$H_2O_2$ (mg/L)** | **T (ºC)** | **pH** | **Time (min)** | **DOC removal** | **$UV_{254}$ removal** | **Parameters** | **Reference** |
|---|---|---|---|---|---|---|---|---|---|---|
| Raw water, Myponga, DOC= 14 mg $L^{-1}$, $UV_{254}$= 55 $m^{-1}$, SUVA= 3.9 L $mg^{-1}$ $m^{-1}$, 54 mg $L^{-1}$ as $CaCO_3$ | LP-UVC, 39 W-, 6-230 J $cm^{-2}$ | 0.9 | 0<br>14 | - | 7.8 | 300<br>180 | 7%<br>35% | 50%<br>98% | DOC, UVabs, $H_2O_2$ concentration, biodegradability, Chlorine demand THMFP, low MW carbonyl compounds, nitrite | Thomson et al., 2004b |
| Raw water, Victoria, DOC= 10.9 mg $L^{-1}$, $UV_{254}$= 25 $m^{-1}$, SUVA= 0.02 L $mg^{-1}$ $m^{-1}$, 34 mg $L^{-1}$ as $CaCO_3$ | LP-UVC lamp, 39 W, 0-250 J $cm^{-2}$ | 0.9 | 0 | - | 7.8 | 300 | 30% | 80% | DOC, UVabs, molecular size distribution, biodegradability | Buchanan et al., 2004 |
| Raw water, DOC= 8 mg $L^{-1}$, $UV_{254}$= 12 $m^{-1}$, SUVA=1.5 L $mg^{-1}$ $m^{-1}$, Alkalinity= 250 mg $L^{-1}$ as $CaCO_3$ | HP, 450 W at 200-700 nm | 8 | 1000 | 25 | 8 | 30 | 90% | - | DOC, residual $H_2O_2$, rate constants, THMFP, molecular size distribution, FTIR, UV spectrum | Wang, 2006 |

| **Water quality** | **Light** | **Volume (L)** | **$H_2O_2$ (mg/L)** | **T (ºC)** | **pH** | **Time (min)** | **DOC removal** | **$UV_{254}$ removal** | **Parameters** | **Reference** |
|---|---|---|---|---|---|---|---|---|---|---|
| Raw water, DOC= 17.4 mg $L^{-1}$, $UV_{254}$= 53.6 $m^{-1}$, SUVA= L $mg^{-1}$ $m^{-1}$, 3 mg $L^{-1}$ as $CaCO_3$ | LP, 48 W | 0.5 | 68 | 20 | 4.54 | 110 | 78% | 94% | DOC, UVabs | Goslan et al., 2006 |
| Raw water, DOC= 1.6 mg $L^{-1}$, SUVA=4 L $mg^{-1}$ $m^{-1}$ | LP,collimated beam, 0-3.5 J/$cm^2$ | 0.07 | 10-20 | | 6.5 | 112 | 7.5% | 30% | DOC, UVabs, THMs, HAAs | Toor and Mohseni, 2007 |
| Raw reservoir water, DOC= 2 mg $L^{-1}$, $UV_{254}$= 8.1 $m^{-1}$, SUVA= 4 L $mg^{-1}$ $m^{-1}$, 2.7 mg $L^{-1}$ as $CaCO_3$ | LP, collimated beam, 0-1.4 J/$cm^2$ | 0.2 | 20 | | 6.5 | - | 0% | 50% | DOC, UVabs, MW distribution | Sarathy and Mohseni, 2007 |
| Nine NOM surrogates, DOC= 3-5 mg $L^{-1}$ | UVC lamp, 39 W-LP, 0-80 J $cm^{-2}$ | 0.9 | 68 | - | - | - | 91% | - | DOC, HAAFP, biodegradation | Bond et al., 2009 |

UV Lamps: LP 185-254 nm; 60 W/$m^2$**;** MP 240-300 nm; 500-2000 W/$m^2$**;** HP 240-300 nm; >2500 W/$m^2$

## 2.3 NOM removal by photocatalytic oxidation

### 2.3.1 $TiO_2$ dark adsorption process

A number of authors have reported significant NOM removal after dark adsorption onto $TiO_2$. Eggins *et al*. (1997) highlighted that 50% of humic acid (1 g $L^{-1}$) was adsorbed measuring $UV_{254}$ absorbance, colour in Hazen and fluorescence after 12 min contact with 1 g $L^{-1}$ of $TiO_2$. The dark adsorption of humic acid (20 mg $L^{-1}$) onto $TiO_2$ (1 g $L^{-1}$) was also studied by Li *et al*. (2002) for 12 h contact time. The results indicated a strong affinity between humic acid and the catalyst at pH 3 (80% removal) which was explained in terms of electrostatic attraction. However, at pH 7 and 9, no adsorption was observed. The authors also reported that the presence of calcium ion was beneficial to the humic acid adsorption at pH 7 maybe due to charge neutralisation. Wiszniowski *et al*. (2002) demonstrated that carboxylate groups were mainly responsible for humic acid adsorption onto $TiO_2$. Liu *et al*. (2008b) further confirmed significant removal of humic acid using only 0.1 g $L^{-1}$ $TiO_2$ in the dark especially at low pH (pH 4) as a decrease from an initial value of 9.4 to 5.7 mg $L^{-1}$ after 15 min contact time was observed. In agreement with Li *et al*. (2002), low adsorption of humic acid at pH 9 was indicated and the key role of electrostatic repulsion was demonstrated using zeta potential measurement.

### 2.3.2 Effect of photocatalytic oxidation on bulk water parameters

A number of papers have reported substantial NOM removal using photocatalytic oxidation process and again many researchers have used humic acid as a model compound (Table 2.3). For example, Bekbolet and Balcioglu (1996) reported complete mineralisation of 50 mg $L^{-1}$ of humic acid after 200 min irradiation (125 W; 0.05 L) and 1 g $L^{-1}$ $TiO_2$ whilst Eggins *et al*. (1997) indicated 100% $UV_{254}$ removal of humic acid (1 g $L^{-1}$) after 60 min irradiation (250 W; 0.1 L) using the same $TiO_2$ dose while DOC removal was only 50%. This shows that performances are dependent on irradiation conditions. This selectivity was confirmed by Han *et al*. (2006) who reported 25% DOC removal using a 15 W irradiation (reactor volume not reported) for 120 min and 2 g $L^{-1}$ $TiO_2$ but over 90% $UV_{254}$ again indicating that that the aromatic components of NOM were easier to treat than achieving mineralisation. Similarly, Liu *et al*. (2008b) reported 95% $UV_{254}$ removal of humic acid after 150 min irradiation (15 W; 0.5 L) and only 0.1 g $L^{-1}$ $TiO_2$ but here and contradictory to Han *et al*. (2006), DOC removal was also significant (95%).

Photocatalytic oxidation of natural raw waters has also shown good performances. Murray and Parsons (2004b) reported 81% and 96% DOC and $UV_{254}$ removals respectively after treatment of high specific UV absorbance (SUVA= 5.1 L $mg^{-1}$ $m^{-1}$) water. SUVA > 4 has been shown to refer to hydrophobic, high molecular weight NOM while SUVA < 2 is more related to hydrophilic, low MW NOM (Edzwald and Tobiason, 1999). In a follow on study, the authors conducted bench and pilot column tests using three reservoir

waters and observed comparable performances (60-77% and 90% DOC and $UV_{254}$ removals respectively) (Murray and Parsons, 2007). Similarly, Le Clech *et al*. (2006) found that 70% of DOC was removed after 120 min irradiation (75 W; 2.5 L) of a low DOC water (2.3 mg $L^{-1}$) in presence of 0.5 g $L^{-1}$ $TiO_2$. This was consistent with the high removals reported by other researchers (Liu *et al*., 2008a; Huang *et al*., 2008; Liu *et al*., 2010). On the other hand, Gerrity *et al*. (2009) reported slightly lower DOC and $UV_{254}$ removals (40% and 76% respectively) using 1 g $L^{-1}$ $TiO_2$ in a 16 L reactor and reported that this was achieved at a treatment energy cost of 5 kWh $m^{-3}$.

### 2.3.3 Parameters affecting oxidation process efficiency

Similarly to UV/$H_2O_2$, photocatalytic oxidation efficiency can be affected by hydroxyl radical scavengers. For example, Bekbolet and Balcioglu (1996) showed that the presence of $HCO_3^-$ carbonate ions (0.1-1 M) was detrimental to humic acid degradation rate. Bekbolet *et al*. (1998) confirmed that the water matrix played a key role in photocatalytic oxidation as chloride, nitrate, sulfate and phosphate anions were shown to retard the degradation rate of humic acid. On the contrary, Li *et al*. (2002) highlighted that calcium or magnesium cations (80 mg $L^{-1}$) enhanced the rate of humic acid removal significantly and showed that after 60 min irradiation, 100% degradation of humic acid was possible in the presence of either of the cations while there was only 50% reduction in absence of cations. This was explained by the fact that adsorption of humic acid

was calcium strength dependent due to electrostatic interaction and calcium ion bridging.

Palmer *et al*. (2002) showed that degradation rate increased with increasing light intensity as the number of oxidising species increased as well. The authors reported relatively low quantum yields (0.003-0.039 mol of carbon per photon).

The extent of mineralisation also depends on pH: for example Palmer *et al*. (2002) reported that the maximum mineralisation of humic acid was observed at pH 7 (over pH 2-12) which was close to the point of zero charge ($pH_{pzc}$) of $TiO_2$. In alkaline conditions, carboxyl and phenolic groups on humic acid will be ionised leading to a negative charge on humic acid molecules, which would result in a repulsion with the increasingly more negative $TiO_2$ ($pH \geq pH_{pzc}$). At acidic pH, carboxyl and phenolic groups on humic acid are uncharged thus enhancing humic acid adsorption onto $TiO_2$ as electrostatic repulsion is reduced. However, aggregation may be a major problem leading to mass transport rate reduction and a lower surface area for light adsorption. On the opposite, Li *et al*. (2002) reported that the highest degradation of humic acid occurred at pH 3 (over pH 3-9) and highlighted the key role of adsorption on the photocatalytic oxidation process. Le Clech *et al*. (2006) found pH 4.5 (over pH 3-8) as optimum pH for the treatment of a low DOC (2.3 mg $L^{-1}$) raw water in a photocatalytic oxidation/membrane treatment. The authors highlighted that the removal efficiency was already high (83%) at natural pH of the raw water (pH=6.5).

$TiO_2$ dose is another key parameter to take into account. Le Clech *et al*. (2006) reported 0.1 g $L^{-1}$ (over 0-0.5 g $L^{-1}$) or 0.04 g per mgC as optimum $TiO_2$ dose (90% TOC removal). A significant TOC removal (63%) was observed in absence of $TiO_2$ showing the effectiveness of the UV system (75 W, low pressure UV lamp). The authors indicated that the light penetration into the bulk solution could weaken at $TiO_2$ dose higher than 0.1 g $L^{-1}$ thus reducing NOM oxidation efficiency. This was confirmed by Huang *et al*. (2008) who demonstrated that photocatalytic oxidation rate constant increased with increasing $TiO_2$ dose up to 0.3 g $L^{-1}$ or 0.03 g per mgC. The $TiO_2$ dose is also directly linked to the geometry of the reactor as shown by Li Puma and Brucato (2007). The optical thickness τ (dimensionless) of a reactor was defined as the product of the thickness of the annulus δ (m), the mass absorption coefficient ε of $TiO_2$ ($m^2$ $kg^{-1}$) and the initial concentration c of $TiO_2$ (kg $m^{-3}$). The determination of the optimum optical thickness thus allows to find the optimum $TiO_2$ dose without performing lengthy experiments.

Photocatalytic oxidation also depends on initial NOM concentration as Huang *et al*. (2008) reported that degradation rate constants decreased from 0.029 to 0.018 $min^{-1}$ with increasing initial TOC content from 5 to 10 mg $L^{-1}$. Since $UV_{254}$ was negligible in both cases, it was suggested that dark adsorption could have a larger contribution at lower TOC concentration. Similar findings were reported by Liu et al. (2010) when comparing the treatment performances of two different Australian surfaces waters at 10.6 and 3.5 mg $L^{-1}$ as DOC respectively.

### 2.3.4 Impact of NOM characteristics

#### *2.3.4.1 Molecular weight (MW) distribution*

A number of authors have shown that photocatalytic oxidation leads to the preferential removal of high MW compounds and the formation of lower MW by-products (Han *et al*. 2006; Le Clech *et al*., 2006; Murray and Parsons, 2007; Huang *et al*., 2008; Liu *et al*., 2008a-b). Liu *et al*. (2008b) suggested that the preferential attack of hydroxyl radicals on larger molecules resulted from the higher number of reaction sites. In another study on two natural raw waters, the authors confirmed the preferential removal of larger molecules (average MW>1000 Da) while molecules in the range of 200-1000 Da were recalcitrant to the process. Espinoza and Frimmel (2009) supported the idea of selective degradation for heterogeneous AOPs such as photocatalytic oxidation using a simple physical model. According to the authors, the selectivity was due to the selective adsorption of NOM onto the $TiO_2$ surface. On the opposite they found no evidence of hydroxyl radical selectivity for UV/$H_2O_2$ systems. This is contradictory to the findings on UV/$H_2O_2$ by Thomson *et al*. (2002b), Thomson *et al*. (2004b), Sarathy and Mohseni (2007).

#### *2.3.4.2 Hydrophobicity*

The impact of photocatalytic oxidation on the hydrophobity of organics has been investigated using the standard resin fractionation technique. This included experiments on both humic acid (Liu *et al*., 2008b) and natural waters (Liu *et al*., 2008a, 2010) where NOM was fractionated into four components: very hydrophobic acid (VHA) composed of high MW humic acid, slightly hydrophobic

acid (SHA) representing fulvic acid, hydrophilic charged (CHA) ascribed to proteins, amino acids and hydrophilic neutral (NEU) attributed to carbohydrates, aldehydes, ketones and alcohols. Liu *et al*. (2008b) showed that high MW hydrophobic VHA fraction decreased after treatment forming low MW hydrophilic charged CHA intermediate by-products which were further degraded at longer irradiation time. On the other hand, NEU fraction which consisted of low MW compounds was found to be the most persistent fraction (Liu *et al*., 2008b). The study on two natural waters (Liu *et al*., 2010) confirmed that hydrophobic fractions were more amenable to oxidation than hydrophilic fraction as aromatics and high MW compounds are more reactive to hydroxyl radicals (Buchanan *et al*., 2005). In agreement with Liu *et al*., (2008b), formation of CHA hydrophilic compounds was reported at the beginning of the treatment before being further degraded while NEU fraction was the most difficult fraction to degrade by photocatalytic oxidation. Similarly, coagulation process was demonstrated to remove preferentially hydrophobic material while hydrophilic material was more recalcitrant (Sharp *et al*., 2006, Bond *et al*. 2010). This implies that NEU fraction is likely to remain in the effluent even if photocatalytic oxidation is combined with coagulation. However it should be noted that this fraction was shown to have a low reactivity to chlorine and should not be an issue in terms of DBP formation.

### 2.3.5 Photocatalytic oxidation by-products

The formation of photocatalytic oxidation by-products has been investigated using mass spectroscopy by Liu *et al*. (2008a) after treatment of a natural water (10 mg $L^{-1}$ as DOC) for 0-240 min (20 W, UVA lamp, 365 nm) and 0.1 g $L^{-1}$ as $TiO_2$. Five carbonyl compounds (formaldehyde, acetaldehyde, acetone, *n*-propanal and *n*-butanal) were identified in the raw water and results revealed that after 150 min of photocatalytic oxidation there was an increase in the formaldehyde and acetone concentration while the longer chain aldehydes compounds such as propanal and butanal were degraded during treatment. Retentions times of the peaks were reported but concentrations of the aldehydes and ketones were not determined. No other study to our knowledge has described the formation of carbonyl by-products after photocatalytic oxidation. However similar by-products have been reported after UV, UV/$H_2O_2$ by Thomson *et al*., (2004b); Sarathy and Mohseni (2009a) as mentioned in section 2.4.

Many authors have investigated the formation of DBPs after photocatalytic oxidation. Richardson *et al*. (1996) observed only a single organic DBP identified as 3-methyl-2,4-hexanedione (50 ng $L^{-1}$) after treatment. When photocatalytic oxidation was followed by chlorination, several chlorinated and brominated DBPs were detected but their number and their concentration were lower than when chlorine was used as a sole disinfectant. For example, THMs and HAAs concentrations were 74.1 µg $L^{-1}$ and 72.2 µg $L^{-1}$ respectively. Liu *et al*. (2008b) reported significant THMFP decrease after photocatalytic oxidation

of humic acid from an initial value of 590 µg $L^{-1}$ to 21 µg $L^{-1}$ after 150 min irradiation (20 W) at pH 7. This was consistent with another study on natural raw water (Liu *et al*., 2008a) where the treatment was shown to reduce the reactivity to chlorine of the NOM as specific THMFP decreased from 56 to 10 µg $mgDOC^{-1}$. The authors also reported 75% HAAFP reduction. However, an increase in trichloroacetic acid (TCAA) from 38 to 49 µg $mgDOC^{-1}$ was indicated at the beginning of the treatment before returning to its initial value with prolonged treatment. In agreement with the two previous studies, Liu *et al*. (2010) highlighted the THMFP reduction of two photocatalytic oxidation treated waters down to < 20 µg $L^{-1}$ showing that the remaining hydrophilic neutral fraction had a low reactivity to chlorine. However, the authors demonstrated an increase in specific THMFP at short irradiation times (30 min; 20 W). This compares well with Gerrity *et al*. (2006) who showed that photocatalytic oxidation treatment (< 5 kWh $m^{-3}$) of a raw surface water resulted in THMFP increase from an initial value of 80 to 140 µg $L^{-1}$. In contrast, extended treatment (< 320 kWh $m^{-3}$) decreased THMFP at energy consumption ≥ 20 kWh $m^{-3}$.

**Table 2.3 Review of experimental conditions and results of photocatalytic oxidation on NOM**

| Water quality | Light | Volume (L) | $TiO_2$ (g/L) | T (ºC) | pH | Time (min) | DOC removal | $UV_{254}$ removal | Parameters | Reference |
|---|---|---|---|---|---|---|---|---|---|---|
| Humic acid, 50 mg $L^{-1}$ | Black Light Fluorescent, 125 W | 0.05 | 1 | - | - | 200 | 100% | 100% | DOC, UVabs, COD, $Color_{400}$, kinetics, effect of $H_2O_2$ and $HCO_3^-$ on degradation rate | Bekbolet and Balcioglu, 1996 |
| Humic acid, 150 mg $L^{-1}$ | Black Light Fluorescent, 125 W | 0.05 | - | - | - | 360 | 100% | 100% | TOC, COD, $BOD_5$, $Color_{400}$, UVabs at 254/280 nm, biodegradability and adsorption on activated carbon | Bekbolet et al., 1996 |
| Humic acid, 1 g $L^{-1}$ | MP Hg lamp, 250 W | 0.1 | 1 | 25 | - | 60 | 50% | 100% | DOC, UVabs at 254/400 nm, fluorescence, COD, $CO_2$ | Eggins et al,. 1997 |

| **Water quality** | **Light** | **Volume (L)** | **$TiO_2$ (g/L)** | **T (ºC)** | **pH** | **Time (min)** | **DOC removal** | **$UV_{254}$ removal** | **Parameters** | **Reference** |
|---|---|---|---|---|---|---|---|---|---|---|
| Humic acid, 0-40 mg $L^{-1}$ | MP Hg lamp, 250W | 0.1 | 1 | 10-68 | 2-12 | - | - | - | Effect of concentration, temperature, oxygen, light intensity and pH on adsorption | Palmer et al., 2002 |
| Reservoir water, DOC= 9.64 mg $L^{-1}$, $UV_{254}$=38.1 $m^{-1}$, SUVA= 5.1 L $mg^{-1}$ $m^{-1}$ | - | 10 | 5 | - | 5 | 60 | 75% | - | Comparison with Fenton's and coagulation, DOC, MW distribution | Murray and Parsons, 2004a |
| Natural water, DOC= 7.5 mg $L^{-1}$, $UV_{254}$=38.1 $m^{-1}$, SUVA= 5.1 L $mg^{-1}$ $m^{-1}$ | - | 10 | 5 | - | 5 | 5 | 81% | 96% | DOC, UV abs, MW distribution, cost per $m^3$ | Murray and Parsons, 2004b |

| **Water quality** | **Light** | **Volume (L)** | **$TiO_2$ (g/L)** | **T (ºC)** | **pH** | **Time (min)** | **DOC removal** | **$UV_{254}$ removal** | **Parameters** | **Reference** |
|---|---|---|---|---|---|---|---|---|---|---|
| Humic acid, 6.7 mg $L^{-1}$ | UVC, 15 W | | 2 | | 3 | 120<br>12 | 30% | 90% | FTIR, NMR, TOC, UV abs, effect of prechlorination on removal | Han et al., 2006 |
| Natural water, DOC= 2.3 mg $L^{-1}$ | LP,75 W | 2.5 | 0-0.5 | 0.3 | 3-8 | 120 | 70% | - | TOC, effects of $TiO_2$ concentration and pH, MW distribution, degradation rate constant | Le Clech et al., 2006 |
| Three natural waters, DOC= 5-24 mg $L^{-1}$, $UV_{254}$=24-106 $m^{-1}$, SUVA= 3.5-5.5 L $mg^{-1}$ $m^{-1}$, 3-10 mg $L^{-1}$ as $CaCO_3$ | - | 0.2-30 | - | - | 3 | 60-90 | 60-77% | 90% | DOC, UV abs, THMFP, MW distribution, Bench and pilot column tests, comparison with coagulation | Murray et al, 2007 |

| **Water quality** | **Light** | **Volume (L)** | **$TiO_2$ (g/L)** | **T (ºC)** | **pH** | **Time (min)** | **DOC removal** | **$UV_{254}$ removal** | **Parameters** | **Reference** |
|---|---|---|---|---|---|---|---|---|---|---|
| Natural water, DOC= 10 mg $L^{-1}$ | UVA, 20 W | 0.5 | 0.1 | - | 7 | 90 | 80% | 100% | DOC, UV abs, addition of $H_2O_2$, MW distribution, fractionation, aldehydes/ ketones, THMFP, HAAFP | Liu et al, 2008a |
| Humic acid, DOC= 10 mg $L^{-1}$ | UVA, 20 W | 0.5 | 0.1 | - | 4-9 | 150 | 80% | 95% | DOC, UV abs, zeta potential, MW distribution, addition of $H_2O_2$ fractionation, THM | Liu et al, 2008b |
| Synthetic water, DOC= 10 mg $L^{-1}$ | LP,8W | 0.75 | 0.3-0.5-1 | 24 | - | 120 | 80% | 100% | TOC, kinetics, adsorption isotherm, effect of initial NOM concentration, MW, UV abs | Huang et al., 2008 |

| **Water quality** | **Light** | **Volume (L)** | **$TiO_2$ (g/L)** | **T (ºC)** | **pH** | **Time (min)** | **DOC removal** | **$UV_{254}$ removal** | **Parameters** | **Reference** |
|---|---|---|---|---|---|---|---|---|---|---|
| Raw river water, DOC= 4.8-7.4 mg $L^{-1}$ , $UV_{254}$=4.6-11 $m^{-1}$, SUVA= 43.5-5.5 L $mg^{-1}$ $m^{-1}$, 105-160 mg $L^{-1}$ as $CaCO_3$ | LP, 75W | 16 | 0.1-1 | - | 7.9-8 | - | 40% | 76% | DOC, UVabs, THMFP, effect of energy consumption $E_{E0}$, chlorine demand, HPSEC | Gerrity et al., 2009 |
| Surface waters, Myponga, DOC= 10.6 mg $L^{-1}$, $UV_{254}$=36.5 $m^{-1}$, SUVA= 3.44 L $mg^{-1}$ $m^{-1}$ | UVA,20 W | 0.5 | 0.1 | - | 7 | 150 | 70% | 100% | DOC, UV abs, molecular weight distribution, fractionation, THMFP | Liu et al. 2010 |

## 2.4 Combination with downstream processes

It is unlikely that AOPs would be used in isolation at a water treatment works and would most likely be used in combination with existing and more conventional water treatment processes such a coagulation, granular activated carbon and biological oxidation. Several countries such as Germany, France, Norway, Austria and Switzerland have adopted UV technology for water disinfection since 1930's. UV plants mostly equipped with medium pressure UV lamps (2-4 J $cm^{-2}$ as UV dose) have been installed in the Netherlands for groundwater disinfection from the 1970's. UV technology has been used for primary disinfection since UV in contrast with chlorine was demonstrated to inactivate *Cryptosporidium parvum oocysts* (Linden *et al*., 2001). This is the case of the city of Seattle (USA) which treats 28,500 $m^3$ per hour since 2002 using a UV dose of 4 J $cm^{-2}$ (Techneau report). The city of New York is also operating low pressure UV lamps for water disinfection. In 2004, a plant based on UV/$H_2O_2$ and designed to operate a daily capacity of 95 000 $m^3$ has been installed in Andijk, the Netherlands. The process achieves 80% degradation of atrazine, a micropollutant, at a UV dose of 5.4 J $cm^{-2}$, 6 mg $L^{-1}$ $H_2O_2$ and 0.56 kWh $m^{-3}$ (Kruithof *et al*., 2007).

Little information has been published on combination of AOPs and other water treatment processes so here we have also tried to draw links to the existing literature on ozonation.

### 2.4.1 Coagulation

In their review, Camel and Bermond (1998) highlighted the often conflicting effects of preozonation on coagulation since preozonation was both reported as beneficial and detrimental to coagulation. Becker and O'Melia (2001) demonstrated that the effect of ozone on coagulation of model waters was dependent on the coagulant type and on the water characteristics that was setting the coagulant dose. For water with moderate or high DOC levels (10 mg $L^{-1}$), the coagulant dose was set by the DOC. Ozonation like UV/$H_2O_2$ and photocatalytic oxidation is known to convert NOM into lower MW by-products and this has been shown to exert a higher coagulant demand than the parent compounds. For low DOC waters (1 mg $L^{-1}$) the authors showed that coagulant dose was set by the particles and the adsorbed NOM and ozone might react with the organics adsorbed on the flocs and alter its conformation to decrease the coagulant demand from 15 to 5 mg $L^{-1}$ as alum dose using 0.5-1 mg $O_3$ per mgC. Uyguner *et al*. (2007) studied the impact of ozonation (3.51 mg $O_3$ per mgC) and photocatalytic oxidation (0.5 g $L^{-1}$ $TiO_2$) on coagulation of humic acid (13 mg $L^{-1}$ as DOC and 118 $m^{-1}$ as $UV_{254}$). After both oxidation treatments, the authors reported < 15% decrease in $UV_{254}$ removal. This compares well with Bose and Reckhow (2007) who showed that preozonation (0.3-1 mg $O_3$ per mgC (equivalent to 30-300 mg $TiO_2$ per mgC for photocatalytic oxidation and 5-10 mg $H_2O_2$ per mgC for UV/ $H_2O_2$ oxidation) of a moderate DOC surface water (3.4 mg $L^{-1}$) led to a decrease in DOC removal. The removal of THM precursors by ozonation combined with coagulation was investigated by Chiang *et al*. (2009). Under optimum conditions (pH 9 and 0.45 mg $O_3$ per mgC) THMFP

removal was increased from 48% versus 60% when compared to coagulation alone (100 mg $L^{-1}$ as alum). It was showed that ozonation was more effective at removing THMFP from hydrophobic fraction (~ 20% removal) than from hydrophilic fraction (~10% removal). The authors therefore suggested that ozonation enhanced THMFP removal by coagulation mostly by reaction with the hydrophobic material. Li *et al*. (2009) demonstrated that the performances of coagulated flocs could be significantly influenced by ozonation due to the variation of organic particles in water. The properties of flocs such as size, fractal dimension and effective density were investigated using laser light scattering and settling column and it was found that suspended particles had not been destabilised by preozonation as zeta potential did not significantly vary. At ozone dose less than 0.53 mg $O_3$ per mgC, floc size was not influenced while at doses > 0.53 mg $O_3$ per mgC flocs were broken and size decreased substantially.

### 2.4.2 GAC adsorption

The use of downstream processes such as GAC is essential after oxidation processes in order to remove the potential by-products such as the low MW carbonyl by-products. Bond *et al*., (2009a) and others have also shown that VUV, UV/$H_2O_2$ can form compounds with significantly higher DBPFP than the parent compounds and this needs to be controlled ahead of chlorine addition.

Many researchers have investigated ozonation in combination with GAC using both batch adsorption isotherm tests and also in pilot scale column tests.

Lambert and Graham (1995) examined the adsorption of upland raw water and commercial humic acid preozonated at 0.19-2.12 mg $O_3$ per mgC by equilibrium adsorption batch tests. The authors suggested that the effects of preozonation on adsorption depended on the nature of the organics. The adsorption of high MW, hydrophobic compounds would be improved by preozonation due to a reduction in MW and addition of complexing functional groups and would not alter the solubility at typical ozone doses. On the contrary, preozonation of low MW, hydrophilic compounds would be detrimental to adsorption as reduction in size and increased functional group would lead to an increase in solubility. On the opposite, Kim *et al*. (1997) found that ozonation of fulvic acid an hydrophobic model compound (5 mg $L^{-1}$) decreased by 20% the adsorbability of the compounds onto GAC. Sanchez-Polo *et al*. (2006) showed that the presence of GAC during ozonation of natural waters had a great potential in NOM removal since activated carbon enhanced the transformation of ozone into hydroxyl radicals. The authors demonstrated that electrons of the graphenic layers (basal plane electrons) and basic surface groups of the activated carbon were the main responsible for the decomposition of ozone into hydroxyl radicals.

Yapsakli *et al*. (2009) conducted batch tests with different types of GAC to investigate the impact of GAC surface properties on adsorption of preozonated NOM at 2 mg $O_3$ per mgC. Results revealed that ozonation did not significantly change NOM adsorption onto thermally GAC but decreased adsorption onto chemically activated carbon. The authors highlighted that surface chemistry (electrostatic interactions for example) was more influential than pore structure.

Chang *et al*. (2002) studied the removal of model aromatic NOM compounds (humic acid, *p*-hydroxybenzoic acid, hydroquinone) by ozone/GAC treatment using GAC columns. As with Lambert and Graham (1995) they found that adsorption of large compounds (humic acid) was improved by preozonation at high doses (6 mg $O_3$ per mgC) and stated this was due to the decrease in MW of the compounds after treatment. Adsorption of the two small compounds (*p*-hydroxybenzoic acid and hydroquinone) was more affected by chemical properties of the compounds: the increase in polarity of the ozonation by-products resulted in a lower adsorbability onto GAC. Kim *et al*. (2005) also investigated ozonation and GAC on a pilot plant (30 $m^3$ per day) that was used to treat a river water source (1.2-2.9 mg $L^{-1}$ as DOC and 2.8-4.2 $m^{-1}$ as $UV_{254}$). When compared to conventional treatment options (coagulation/sand filtration/GAC), the integration of ozonation (1 mg $O_3$ per mgC) as a pretreatment to GAC did not show any enhancement of either DOC or $UV_{254}$ removal which were 60% and 80% respectively. Ozonation did not show any benefit for DBP control either as the total concentration of HAA and THM formed were less than 50 µg $L^{-1}$ with and without ozonation in the flowsheet. Kim *et al*. (2006) examined NOM hydrophobicity after ozonation and GAC on a pilot plant (40 $m^3$ per day) and reported that the hydrophilic fraction was selectively adsorbed onto GAC while hydrophobic fraction was more degraded by ozonation. It was suggested that the activated carbon surface became more hydrophilic due to the formation of oxygenated ozonation by-products. Surprisingly biological activity on the GAC was not taken into account although the experiment was 10 month long. In a following paper (Kim and Yu, 2007), the

authors studied the formation of oxygenated ozonation by-products and showed that ozonation did not oxidise the carboxylic fraction (from 39.1 to 35.9%) while GAC removed some of the carboxylic fraction (from 35.9 to 29.1%).

### 2.4.3 Biotreatment

Apart from sterile GAC, biological treatment (in biologically activated carbon (BAC)) have been widely studied as an AOP downstream process since biological degradation is likely to predominate in GAC adsorbers after extented treatment (Toor and Mohseni, 2007; Buchanan *et al*. 2008). As in the case of virgin GAC, the most described process in the literature was ozonation. For example, Graham (1999) reviewed the various investigations concerning humic rich waters treatment by ozone and biological filtration (slow sand filtration and activated carbon filtration) and showed the benefits and limitations of such combination of processes. Yavich *et al*. (2004) used the concept of rapidly and slowly biodegradable NOM and showed that ozonation of waters containing high DOC content (9-11 mg $L^{-1}$) resulted in increased concentration of both rapidly and slowly biodegradable NOM. However, the slowly biodegradable NOM was difficult to remove by conventional biofiltration and could lead to bacterial regrowth in the distribution system. The authors proposed the idea of a stimulated biodegradation by adding an easily biodegradable carbon source in the water. On the other hand, Teksoy *et al*. (2008) highlighted that biodegradable NOM could increase THM levels as a strong correlation between BDOC and THMFP was reported after ozonation of a raw humic rich water (4.1

mg $L^{-1}$ as DOC and 10 $m^{-1}$ as $UV_{254}$). Thomson *et al*. (2002a) investigated the effect of UVC radiation on biodegradability of a raw reservoir water (9.5 mg $L^{-1}$ as DOC) and reported that biodegradability was unchanged at UV doses < 1 J $cm^{-2}$ but increased at higher doses (10-26 J $cm^{-2}$). The authors also demonstrated that chlorine consuming oxidation by-products were biodegradable and that biotreatment removed preferentially low MW compounds. This is consistent with Bond *et al*. (2009a) who reported that amino acids (L-glutamic acid, L-aspartic acid, glycine, L-leucine, L-serine) were effectively removed by biotreatment but HAAFP increased moderately. In another paper (Buchanan *et al*., 2004), UV irradiation of a raw water (10.6 mg $L^{-1}$ as DOC) increased BDOC content from an initial value of 15% of the total DOC to 40% at 140 J $cm^{-2}$. A good correlation between $UV_{254}$ decrease and BDOC increase was found showing that biodegradable oxidation by-products resulted from the breakdown of chromophoric material. They also showed that vacuum UV at 32 J $cm^{-2}$ led to 36% BDOC highlighting the better efficiency of AOPs compared with direct UV photolysis.

Combination of AOPs with downstream biological activated carbon (BAC) columns has been studied by a number of researchers. For example, Toor and Mohseni (2007) showed the synergetic effects of UV/$H_2O_2$ at moderate UV and $H_2O_2$ doses (5 J $cm^{-2}$ and 20 mg $L^{-1}$) combined with BAC process and reported 43%, 52% and 59% reduction in DBPs, DOC and $UV_{254}$ respectively. Furthermore, the authors highlighted that AOP-BAC combination did not affect the biostability of the water. Similarly, Buchanan *et al*. (2008) studied the combination of VUV process at 16 J $cm^{-2}$ with BAC columns in the case of a

raw surface water (6.9 mg $L^{-1}$ as DOC and 16 $m^{-1}$ as $UV_{254}$) and reported 44%, 60-70% and 74% as DOC, THMFP and HAAFP removals respectively after 60-90 days treatment. Xu *et al*. (2007) also indicated significant benefits of $O_3$-BAC process in a pilot scale study of a river water (5.2-7.7 mg $L^{-1}$ as DOC and 9.9-19.2 $m^{-1}$ as $UV_{254}$) as 60% DOC removal was achieved versus 31% with ozonation alone. THMFP and HAAFP removal reached 70% and 50% respectively after $O_3$-BAC while conventional processes achieved only 20% THMFP and HAAFP reduction. Results also showed no genetoxicity in the BAC effluent.

Treguer *et al*. (2009) coupled ozonation (1 mg $O_3$ per mgC) with a hybrid membrane bioreactor containing fluidised activated carbon (powdered activated carbon - PAC) to treat a river raw water (2.1-3.1 mg $L^{-1}$ as DOC and 3-6 $m^{-1}$ as $UV_{254}$). Batch experiments confirmed that ozonation enhanced BDOC from an initial value of 0.3 mg $L^{-1}$ to 0.7 mg $L^{-1}$ at 1 mg $O_3$ per mgC. This dose was chosen for pilot scale experiments during 4.5 months to favour biodegradation to the detriment of adsorption onto PAC. Results revealed that BDOC only increased by 0.2 mg $L^{-1}$ instead of 0.4 mg $L^{-1}$ found in batch tests implying that only 50% of the available BDOC was effectively removed. It was also shown that the non-adsorbable DOC fraction (40% of the total DOC) was refractory to biodegradation. Yapsakli and Cecen (2010) investigated the effects of two different GAC types (thermally activated and chemical activated) on biodegradation of preozonated raw reservoir water (3.5-5.8 mg $L^{-1}$ as DOC). Biological activity was shown to increase the bed life of the BAC filters and DOC removal was higher in thermally GAC columns than in chemically GAC

columns. The authors showed that adsorption onto GAC and biodegradation were correlated. In agreement with Treguer *et al*. (2009) ozonation did increase BDOC but the combination with BAC columns did not show any significant benefit compared with BAC alone. For low SUVA waters exhibiting high biodegradability, preozonation could be eliminated as long as retention time in BAC columns is sufficient to remove the slow biodegradable organics.

## 2.5 Summary

$UV/H_2O_2$ and photocatalytic oxidation based AOPs have both shown significant benefits in NOM removal and also DBP control. Clear differences between the two processes have been reported which may be linked to the formation of other reactive species (such as superoxide radical) than hydroxyl radicals or the significant role of adsorption onto $TiO_2$ in the case of photocatalytic oxidation. Humic material in particular has been shown to have a high affinity with $TiO_2$. It is clear that the performances of both processes as a treatment option are dependent on the NOM characteristics. In general, humic rich waters composed of high MW, hydrophobic compounds were easier to treat by $UV/H_2O_2$ and photocatalytic oxidation than low MW, hydrophilic compounds. The impact of the water matrix was also to take into account as hydroxyl radical scavengers such as carbonate species could affect the process efficiency. UV dose or treatment time was correlated with the extent of NOM degradation but complete mineralisation was rarely reported even at high UV doses (> 200 J $cm^{-2}$). In terms of chlorine reactivity, treatment time was a key parameter as short

irradiation time resulted in an increase in DBPFP while only longer irradiation time could lead to DBPFP reduction showing the necessity of optimising the process. UV/$H_2O_2$ and photocatalytic oxidation had both the same impact on NOM structure as a shift towards more hydrophilic low MW species and a significant reduction of aromaticity and double bonded character were observed. This was supported by the identification of low MW carbonyl by-products such as aldehydes, ketones and carboxylic acids. However few studies evaluated the potential toxicity of these oxidation by-products even if their concentrations were low (< 1 µg $L^{-1}$).

It is worth noting that a number of researchers have studied humic acid as a NOM model compound instead of natural raw waters as the use of model compounds allows a better understanding of the impact of NOM properties on reactivity. In such studies the influence of the water matrix is usually not considered. Humic acid studies confirmed the substantial benefits of treating high MW, hydrophobic compounds by UV/$H_2O_2$ and photocatalytic oxidation. However few studies have investigated the AOP treatment of other NOM model compounds such as amino acids or carbohydrates to date.

As it is likely that an AOP will be combined with existing conventional processes, we reviewed the combination of AOP (and ozonation) with coagulation, GAC and biotreatment. The combination of AOPs with coagulation (especially in the case of ozonation) showed contradictory effects on NOM removal which mainly depended on the ozone dose. Adsorption of organics onto fresh GAC was both affected by size and surface chemistry. Most studies

reported no significant benefit of AOP pretreatment onto fresh GAC adsorption. On the other hand, biodegradability was substantially enhanced after treatment highlighting the potential of downstream BAC. Oxidation by-products were efficiently removed by such downstream process. However, the existence of slowly biodegradable NOM and refractory NOM could be an obstacle to the efficiency of AOP-BAC combination.

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# 3 UV/$H_2O_2$ treatment of an hydrophilic natural organic matter rich reservoir water and its combination with coagulation, adsorption and biodegradation processes

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## 3.1 Abstract

This study evaluated the UV/$H_2O_2$ treatment of an hydrophilic rich high alkalinity water at UV doses up to 6 J $cm^{-2}$ and 2 mM $H_2O_2$. Results showed non purgeable organic carbon (NPOC) and UV absorbance at 254 nm ($UV_{254}$) removals of 26% and 76% respectively. Significant structural changes of the NOM were observed: loss of aromaticity and conjugated double bonded species, shift towards lower molecular weight species, formation of oxygenated by-products. Trihalomethane formation potential (THMFP) was found to increase by 67% after 3 J $cm^{-2}$ and 1 mM $H_2O_2$ while it was reduced by 34% after 6 J $cm^{-2}$ and 1 mM $H_2O_2$. UV/$H_2O_2$ was combined with traditional

processes such as coagulation, granular activated carbon (GAC) and biotreatment and the investigation revealed limited benefits or reduction in performance linked to the change in character of the organics. GAC columns tests revealed moderate benefits in terms NPOC and THMFP capacity and enhanced biotreatment at high UV doses (6 J $cm^{-2}$). Overall the study suggests that the application of advanced oxidation processes with high alkalinity, highly hydrophilic waters needs careful consideration and that UV dose is a key parameter to take into account in relation with by-product formation so that tailored solutions can be developed.

## 3.2 Introduction

Advanced oxidation processes have for a number of years been proposed as alternative treatment processes to conventional oxidants such as chlorine and ozone (Comninellis *et al*. 2008). The UV/$H_2O_2$ process in particular is now considered a competitor with ozonation when considering treatment of surface or ground waters polluted with pesticides. The process is relatively simple and is based on the direct photolysis of $H_2O_2$ molecules to generate hydroxyl radicals (•OH). These radicals have been widely reported to be powerful yet unselective oxidant and have been successfully shown to treat a wide range of important trace organic pollutants (Dotson *et al.*, 2010). There remains a limited number of studies on the application of advanced oxidation processes for the treatment of bulk organics in waters or wastewaters. The majority of studies have considered the application of UV/$H_2O_2$ for natural organic matter removal

and the impact that oxidation has on disinfection by-products (DBPs) formation. Wang *et al*. (2006) for example reported the oxidation of a humic acid solution with UV (450 W high pressure lamp) and showed 92% and 80% removal of dissolved organic carbon (DOC) and trihalomethane formation potential (THMFP) respectively after 30 min UV irradiation and 1100 mg $L^{-1}$ of $H_2O_2$. Goslan *et al*. (2006) showed similar findings (DOC and $UV_{254}$ removals of 94% and 78% respectively) but for a high DOC (17.4 mg $L^{-1}$) surface water. In all these studies complete mineralisation of the NOM by UV/$H_2O_2$ has not been achieved even at UV fluences up to 200 J.$cm^{-2}$ but it is clear that treatment does affect the structure of the organics leading to a decrease in molecular weight and a loss of aromatic character (Sarathy and Mohseni, 2009).

Investigations into the likely by-products formed during UV/$H_2O_2$ treatment have shown the production of low molecular weight carbonyl by-products such as oxalic acid, acetic acid, malonic acid and butanoic acid (Backlund, 1992). Thomson *et al*. (2004) reported the formation of formaldehyde (~30 µM), acetaldehyde (~30 µM) and 0.5-3 µM of glyoxal, methyl glyoxal and glyoxylic acid after 45-180 min of UV-C irradiation (39 W) and 14 mg $L^{-1}$ of $H_2O_2$. As with ozonation processes there is a need for downstream treatment processes to remove these oxidation by-products as they could present a potential health concern (Parkinson *et al*., 2001), enhance chlorine demand or contribute to biofilm formation in the distribution system (Thomson *et al*. 2004). In addition these organics have been shown to be more reactive with chlorine leading to more disinfection by-products such as trihalomethanes and haloacetic acids (Kleiser and Frimmel, 2000; Mohseni, 2007; Bond *et al*., 2009a).

The impact of ozonation on downstream treatment processes has been extensively studied and conflicting results have been reported and it is likely that many synergies exist between these results and what may occur after oxidation with AOPs (Camel and Bermond, 1998). For instance, Becker and O'Melia (2001) demonstrated that the effect ozone had on coagulation were dependent on both the coagulant type and the water quality characteristics. For high or moderate DOC waters, the coagulant dose was controlled by the DOC concentration in which case the impact of the ozone was detrimental For low DOC waters, the coagulant dose was controlled by the concentration of particles and in these cases ozone had a positive effect and reduced the coagulant dose required to treat the water. Bose and Reckhow (2007) reported that ozonation of hydrophilic NOM was beneficial to the adsorption of these organics onto aluminium hydroxide flocs. The authors proposed a two stage coagulation process with intermediate ozonation where the humic fraction would be removed by the first coagulation stage while the second coagulation stage would target the non-humic fraction. A number of studies have also highlighted the efficiency of a ozonation and biotreatment combination to control disinfection by-product formation (Speitel *et al*., 1993; Graham, 1999; Treguer *et al*., 2009) while other researchers have investigated the enhanced biodegradability after UV and vacuum UV (Thomson *et al*., 2002; Buchanan *et al*., 2008). A recent study reported by Toor and Mohseni (2007) showed promising results after UV/$H_2O_2$ and biological activated carbon (BAC) treatment where 43%, 52% and 59% reduction in TOC, $UV_{254}$ and DBPs respectively were observed.

If we consider where advanced oxidation processes are most likely to feature for bulk organics removal it is those that sites which currently experience limited TOC removal during coagulation that are most highly ranked (Comninellis *et al*., 2008). This tends to reflect waters with high alkalinity that contain highly hydrophilic, low charged organics as such characteristics limit the effectiveness of the coagulation process (Sharp *et al*., 2006a; Duan and Gregory, 2003). In fact recent studies have shown a direct correlation between the raw water hydrophilic content and the minimum possible organics residual meaning that even under optimum conditions coagulation may not be sufficient (Sharp *et al*., 2006b). In all cases maximum DOC removal occurs where charge based coagulation is maximised which requires low pH (e.g. 4.5 for Ferric; 6 for Alum) operation to keep the coagulant hydrolysis products highly cationic (Henderson *et al*., 2006). In high alkalinity waters, the cost associated with pH correction limits this option and so coagulation is normally performed under sub optimal conditions limiting DOC removal. Consequently, such waters offer a potential application for advanced oxidation processes (Comninellis *et al*., 2008) however, whilst operation for complete mineralization remains uneconomic, there is a need to understand the impact of the advanced oxidation process on the rest of the treatment flowsheet. The current paper aims to contribute towards this and add to the existing knowledge on the impact of ozonation by considering the case of UV/$H_2O_2$ as part of a treatment scheme for a real, high alkalinity, highly hydrophilic water. A number of possible flowsheets have been considered: UV/$H_2O_2$ as a pre or post-treatment to coagulation, coagulation/UV/$H_2O_2$/GAC and coagulation/UV/$H_2O_2$/biotreatment in order to

understand how the adoption of an advanced oxidation process would influence the downstream processes typically employed in potable water treatment.

## 3.3 Materials and methods

### 3.3.1 Water samples

The raw and coagulated waters were collected in October 2006 from a surface water treatment works in the Severn Trent Water region, UK. The water is characterized as having a high alkalinity (170-180 mg $CaCO_3$ $L^{-1}$), moderate NPOC (5.3 $mg.L^{-1}$) which is a mix of hydrophobic and hydrophilic organic compounds as indicated by a SUVA of 2.5 $m^{-1}$ $mg^{-1}$ L and has a low turbidity (0.6 NTU). The raw water is treated through a combination of coagulation, sedimentation, filtration and activated carbon adsorption. Coagulation on site is conducted at pH 7.6 by dosing ferric sulphate at a rate of 5 mg $L^{-1}$ as Fe leading to an average reduction of 50%. Water was sampled from both the raw water intake and post-clarified outlet for subsequent testing in the Cranfield University laboratories. A series of treatment schemes were tested based on combinations of UV/$H_2O_2$ and coagulation, adsorption and biotreatment (Table 3.1 and Figure 3.1).

**Table 3.1 Treatment options tested during the investigation**

| Scheme | Source Water | Treatment train | Conditions |
|---|---|---|---|
| A | Raw water | Coagulation | 2-10 $mg_{Fe}.L^{-1}$ at pH 4.5 and 7.6 |
| B | Raw water | UV/$H_2O_2$+coagulation | Collimated beam 0-6 J $cm^{-2}$, 0-2 mM $H_2O_2$ |
| C | Raw water | Coagulation+UV/$H_2O_2$ | Collimated beam 0-6 J $cm^{-2}$, 0-2 mM $H_2O_2$ |
| D | Coagulated water | UV/$H_2O_2$+GAC | UV reactor, 0-6 min RT, 0-2 mM $H_2O_2$ |
| E | Coagulated water | UV/$H_2O_2$+biotreatment | UV reactor, 0-6 min RT, 0-2 mM $H_2O_2$ |

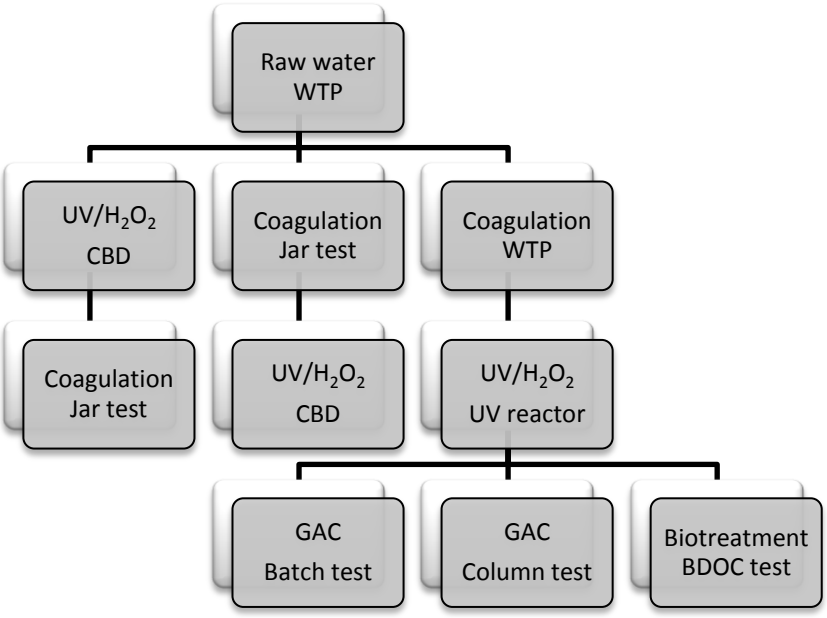



**Figure 3.1 Process sequences (WTP: water treatment plant; CBD: collimated beam device)**

### 3.3.2 UV/$H_2O_2$

A collimated beam device (Wedeco, AG, Germany) (Figure 3.2) with four low pressure UV lamps of 30 W emitting at 254 nm was used to evaluate the effects of UV/$H_2O_2$ on the characteristics of the water and during scheme B and C. In each case, 250 mL sample was placed in a Petri dish (19.7 cm in diameter) positioned at a distance of 40 cm from the UV lamps and constantly mixed with a magnetic stirrer. The UV dose ranged from 0 to 6 J $cm^{-2}$. The UV dose (in J $m^{-2}$) was calculated as the product of the treatment time (seconds) by the average UV irradiance (in W $m^{-2}$) (Bolton and Linden, 2003) with the average UV irradiance calibrated as 22.6 W $m^{-2}$ by uridine actinometry (Von Sonntag *et al*., 1992). Lamps were allowed to warm for 15 minutes before beginning the experiments and temperature was maintained at 20°C in an air conditioned laboratory.

In all other schemes (D-E) a batch photochemical reactor (Model Products Ltd, Cranfield UK) consisting of a 8L stainless steel vessel containing four low pressure mercury vapour UV lamps (UVMax Model C, Trojan Technologies Inc., Canada) of 43 W each emitting at 254 nm was used and kept well mixed through use of a vertically mounted impellor (Figure 3.3). Due to the complexity of the UV dose calculations in the reactor, irradiation was evaluated in function of time and ranged from 0.5 to 6 min. Prior to UV irradiation in both devices, $H_2O_2$ doses of 0 to 2 mM (0-68 mg $L^{-1}$) were added to the water samples with quantification of the $H_2O_2$ concentration achieved using the iodometric method (Klassen *et al*., 1994). After irradiation, residual $H_2O_2$ was quenched by bovine liver catalase (lyophilized powder, > 10 000 units $mg^{-1}$ protein, Sigma-Aldrich, UK) at a dose of 0.2 mg $L^{-1}$. For NPOC analysis, 1 mg $L^{-1}$ of residual $H_2O_2$ was quenched by sodium sulfite $Na_2SO_3$ (Fisher Scientific, UK) at 3.7 mg $L^{-1}$ since catalase was found to increase significantly the NPOC values of the samples. The optical thickness τ of the reactor defined as the product of the thickness of the annulus δ (10 cm), the mass absorption coefficient ε of $H_2O_2$ (1284 $m^2$ $kg^{-1}$) and the initial concentration c of $H_2O_2$ (0.017 kg $m^{-3}$) was found to be equal to 2.18. This value compares well with the range 1.8-4.4 reported by Li Puma and Brucato (2007) in the case of a flow-through photocatalytic reactor.

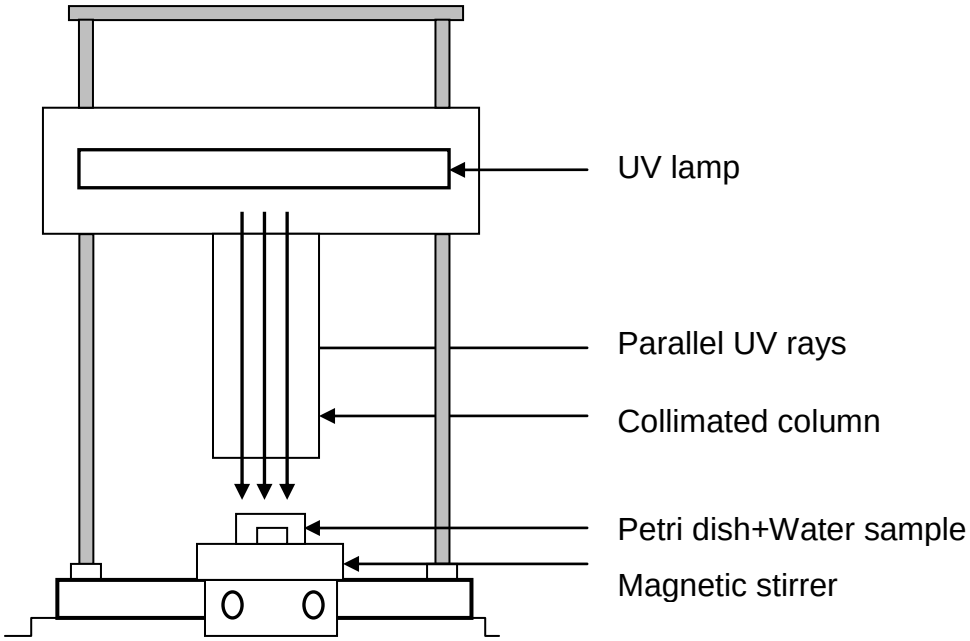



**Figure 3.2 Collimated beam device**

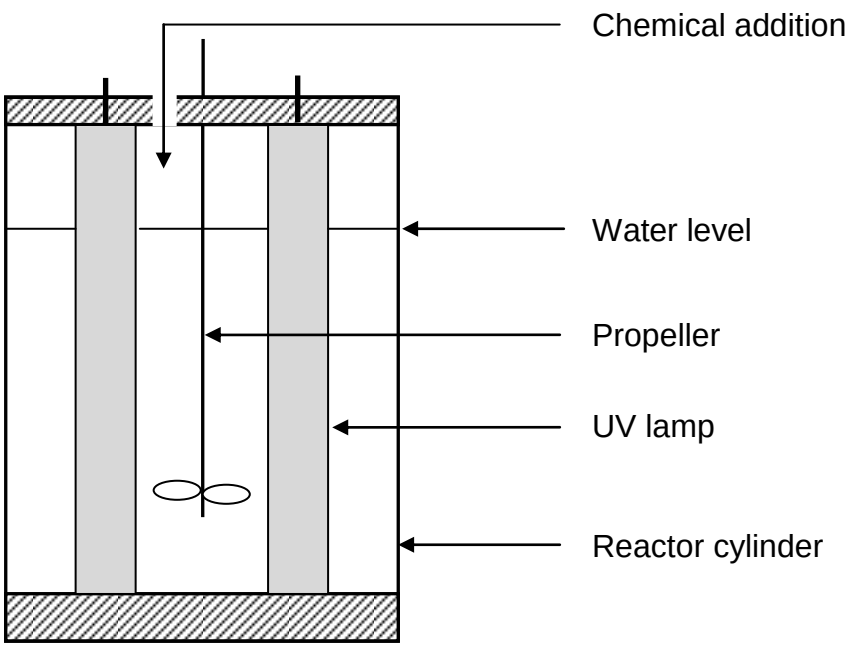



**Figure 3.3 UV batch reactor**

### 3.3.3 Coagulation jar test

Coagulation experiments were conducted using a standard jar tester (Phipps and Bird PB-900, Virginia, USA) consistent with the approach described by Sharp *et al*. (2006a) where 500 mL of water was placed into each jar with ferric sulphate (Ferripol xl, EA West) as coagulant at a dose of 2 to 8 mg $L^{-1}$ as Fe during the initial rapid mix phase (2 minutes at 200 rpm). HCl (1 M) (Fisher Scientific, UK) was then added until the pH was adjusted 7.6 (corresponding to the pH used at the water treatment works) whilst stirring for an additional 1.5 minutes at 200 rpm. The jars were then stirred for 15 minutes at 30 rpm and left to settle for an additional 20 minutes prior to sample collection.

### 3.3.4 Granular activated carbon adsorption

Batch tests were performed by adding varying carbon doses between 0 and 2 g into 250 mL of the water samples which were then stirred continuously on an orbital shaker (New Brunswick Scientific) at 200 rpm for 24 hours at 20°C. Water samples were then filtered (0.2 µm, Fisher Scientific, UK) prior to analysis. Granular activated carbon (Filtrasorb 400, Chemviron, UK) was used throughout and was crushed and sieved between 32 and 106 µm, washed thoroughly in deionised water, dried overnight at 110°C and kept in a dessicator prior to use. Given that natural humics materials were targeted, a modified form of the Freundlich isotherm was used due to the multicomponent character of the NOM which cannot only be described as a function of the liquid-phase

equilibrium concentration. However a unique mixture isotherm, linear on log-log coordinates, can be obtained when capacity is plotted as a function of the non-adsorbed NOM per unit carbon mass ($C_e/D_o$):

$$q_e = K_F \left( \frac{C_e}{D_o} \right)^n$$

where: $q_e$ is the amount adsorbed at equilibrium (normalised to adsorbent mass), $c_e$ is the equilibrium solution phase concentration, $K_F$ is the Freundlich parameter for a heterodisperse system, and the exponential term $n$ is related to the adsorption force and the energy of sites on the surface of the adsorbent.

Kinetic experiments were performed in a rapid small scale column tests (RSSCT) according to standard practice (ASTM D6586-03) (Table 3.2). A mass of 4 g of GAC was used for all runs. The GAC was sized to 150-200 µm and boiled in ultrapure water for 10 minutes in order to replace the air in the carbon pores with water. The set-up consisted of a metering pump (Watson Marlow Ltd, UK), a pressure indicator (Excel Pneumatics, UK) and a glass column (1 cm x 50 cm, Kinesis Ltd, UK) into which the 4 g of carbon were placed. The empty bed contact time (EBCT) was set at 2.5 min and the water pre-filtered using a 0.4 µm chlorinated polyethylene (PE) membrane (Kubota, Japan). Samples were taken at regular intervals and analysed for NPOC, THMFP and $UV_{254}$ according to the methods stated below. Samples were analysed immediately when possible or stored at 4°C until the analysis was performed which was no more than 72 h after collection.

**Table 3.2 RSSCT parameters**

| Parameter | Units | RSSCT |
|---|---|---|
| Flowrate | mL $min^{-1}$ | 5 |
| Bed Volume | mL | 12.5 |
| EBCT | min | 2.5 |
| GAC particle diameter | mm | 0.15-0.2 |
| Hydraulic loading | m $h^{-1}$ | 3.8 |

### 3.3.5 Biotreatment

The biodegradability of the samples was assessed using the method described by Joret and Levi (1986) where 250 mL of water is incubated for 8 days with 50 g of filter sand. The sand was collected from the Severn Trent Water treatment works and was stored in raw water with constant aeration. The bioactivity of the sand was verified using sodium acetate (Fisher Scientific, UK) as a positive control. Biodegradable dissolved organic carbon (BDOC) is defined as the difference between the initial NPOC and the minimum NPOC value after 5-8 days.

### 3.3.6 Analysis

#### *3.3.6.1 Fractionation*

Amberlite XAD-7HP and Amberlite XAD-4 resins (Rohm and Haas, PA, USA) were used to fractionate 500 ml water samples and obtain three different fractions: hydrophobic, transphilic and hydrophilic. Each type of resin (1.5 L) was slurried with NaOH (0.1 M; 1.5 L) for 24 hours. The resin was sequentially Soxhlet extracted for 48 hours each with methanol, acetonitrile and methanol again (1.8 L). The resin was packed into glass columns and rinsed with reverse osmosis (RO) water until the column effluent DOC was less than 2 mg/L. Each column (resin volume = 8 mL) was rinsed with NaOH (0.1 M), followed by ultrapure water and finally HCl (0.1 M). Water samples were filtered (0.45 µm, Fisher Scientific, UK) and acidified to pH 2 using HCl. The samples were then passed through the XAD-7HP column where the hydrophilic fraction was collected at the effluent. The XAD-7HP effluent was then passed through the XAD-4 column where the transphilic fraction was collected. DOC of the initial water sample and the two effluents (hydrophilic and transphilic) were measured and the abundance of hydrophobic fraction was determined by mass balance as the fraction did not elute from the XAD-7HP resin. All the chemical solutions and solvents were supplied by Fisher Scientific, UK.

#### *3.3.6.2 Charge determination*

Charge concentration was determined following an adapted method described by Sharp *et al*. (2006a) where the charge is measured as a function of cationic polymer polydiallyldimethylammonium chloride or polyDADMAC (Sigma Aldrich,

20% wt) concentration. A beaker containing 100 mL of water sample, set at pH 7, was stirred using a magnetic stirrer while varying amounts of polyDADMAC (as 0.01% solution) were added to the beaker. After each addition of polyDADMAC, the zeta potential was measured by the Zetasizer (Malvern, UK) until the point of zero charge or isoelectric point (i.e.p.) had been identified.

*3.3.6.3 Bulk parameter analysis*

A Shimadzu 5000A TOC analyser was used for determining NPOC content. Samples were acidified with 1% HCl (2 M) and purged for 6 minutes. NPOC values reported here represent the average of three samples, each measured twice. UV absorbance was measured at 254 nm wavelength using a Jenway 6505 UV/Vis spectrophotometer. The device was calibrated daily using deionised water. All samples were passed through a 0.2 µm filter paper (Fisher Scientific, UK) and stored at 4 °C prior analysis. $UV_{254}$ values reported here represent the average of three samples, each measured three times. Error bars represent the standard deviation between the average measurements for three samples. Size exclusion chromatograms were determined using a HPLC (Shimadzu VP series, Shimadzu, Milton Keynes, UK). Fluorescence Excitation Emission Matrix (EEM) measurements were performed using a Vary Cary Eclipse Spectrophometer (Middleburg, The Netherlands) at room temperature of 20 ºC. The equipment was auto-zeroed prior to each analysis. Raman signal of water was recorded as a quality control on a daily basis. EEM spectra were generated by scanning excitation wavelengths from 250 to 450 nm with 5 nm steps and detecting the emission wavelengths between 275 and 500 nm with 5

nm steps. The IR spectra were obtained by scanning NOM pellets in FT-IR spectrophotometer ThermoNicolet Avatar 370. The pellets were composed of NOM powder obtained through freeze drying water samples. The powder was mixed with KBr in the ratio of 1:30 and heated to 80 ºC before being pressed.

THMFP was measured following an adapted version of USEPA Method 551.1. Samples were buffered to pH 7 with phosphate buffer solution. Chlorine was added in excess as sodium hypochlorite (Fisher Scientific, UK) at a dose of 5 mg $Cl_2$ per mg C. Chlorinated samples were incubated at 20 ºC for 24 hours in the dark in headspace-free 100 mL PTFE bottles. At the end of the reaction time, residual chlorine was quenched with sodium sulfite (Fisher Scientific, UK). THMs were extracted and derivatised with 3 mL of methyl tertiary-butyl ether (MTBE) at pH 4.5-5.5 and 10 g of sodium chloride (both Fisher Scientific, UK). The sample was shaken for 3-5 min manually. Once settled, the top layer was finally transferred to an autosampler vial and THMs were measured using a gas chromatograph with micro electron capture detector (Agilent 6890 GC-ECD). The instrument conditions were as follows. A capillary column (ZB-1MS column (Phenomenex, UK) 30 m × 0.25 mm × 0.25 µm) was used with ultra high purity helium carrier gas at a constant linear velocity of 25 cm $s^{-1}$. The detector make-up gas was nitrogen at a flow rate of 30 mL $min^{-1}$. The split ratio was set at 10:1. A volume of 1 µL was injected. The initial oven temperature was 35 °C held for 22 minutes followed by a 10 °C per minute temperature ramp to 145 °C and held for 2 minutes. The temperature was increased to 225 °C at a rate of 20 °C per minute and held for 15 minutes followed by an increase to 260 °C at a rate of 10 °C per minute and held for 30 minutes. The temperature of the

injector was set at 200°C and the detector at 290°C. The rate of data collection was 20 Hz. Bromofluorobenzene at 30 µg $L^{-1}$ was used as internal standard. All chemicals were analytical grade or higher. Standards for THMs were available from Sigma Aldrich Ltd (UK). Limit of detection (LOD) was 0.052 µg $L^{-1}$ and minimum reporting level (MRL) was 0.157 µg $L^{-1}$. Values reported here represent the average of two samples, each analysed twice.

## 3.4 Results and Discussion

### 3.4.1 The impact of UV/$H_2O_2$ on bulk parameters and chlorine reactivity

The application of UV/$H_2O_2$ resulted in a decrease in NPOC from a raw water value of 5.3 mg $L^{-1}$ to 4.9, 4.1 and 3.9 mg $L^{-1}$ with the addition of 1 mM $H_2O_2$ and UV doses of 1, 3 and 6 J $cm^{-2}$ respectively (Table 3.2). No significant difference was observed for $H_2O_2$ doses between 0.5 and 2mM (17-68 mg $L^{-1}$) indicating that over the conditions trialed, UV was the reaction limiting component for the advanced oxidation process. The choice of $H_2O_2$ dose was based on previous work by Goslan *et al*. (2006) who used the same irradiation device as we did. Considering the stoichiometric reaction between 1 mM of $H_2O_2$ and NOM based on DOC content (6 mg $L^{-1}$) enables to predict 0.8 mM excess of $H_2O_2$. Direct photolysis over the same dose range resulted in no significant change to the bulk characteristics of the water which is consistent with previous reports which have shown less than 10% DOC reduction after

irradiation of up to 10 J $cm^{-2}$ (Thomson *et al.*, 2002b) and indicates that advanced oxidation reactions are necessary to generate an alteration in the water quality. Corresponding removal levels in relation to $UV_{254}$ were much higher at 39%, 65% and 75% for UV doses of 1, 3 and 6 J $cm^{-2}$ respectively demonstrating that the oxidative reactions preferentially target $UV_{254}$ absorbing compounds resulting in preferential decrease in aromaticity and conjugated double bonded species. Comparison to previous studies suggests performance is related to raw water character. For instance, in the case of a low alkalinity, high DOC (17.4 mg $L^{-1}$), high UV(53.5 $m^{-1}$) and low turbidity water typical of moorland catchments in the UK, 8 J $cm^{-2}$ (UV-C, 200-280 nm) and 50 mg $L^{-1}$ of $H_2O_2$ produced a 50% reduction in DOC (Goslan *et al.*, 2006). Whereas, application of 1.4 J $cm^{-2}$ and 20 mg.$L^{-1}$ resulted in only 15% reduction in the DOC of water sourced from the Capilano reservoir (Sarathy and Mohseni, 2007; 2009). This was similar to 4% observed after applying a dose of 23 J $cm^{-2}$ from a low pressure UV on a low alkalinity reservoir water (DOC= 10 mg $L^{-1}$) (Buchanan *et al.*, 2005). The main differences in the studied waters were the initial DOC, the hydrophobicity and alkalinity. Previous work with NOM surrogates was unable to find a direct link between hydrophobicity and reaction with •OH suggesting that a balance of factor is important (Bond *et al.*, 2009a) including the scavenging effect of the water matrix. In the current case the water had a significant alkalinity (180 mg$CaCO_3$ $L^{-1}$) which has been shown to be detrimental to organics degradation by hydroxyl radicals (Wang *et al*., 2000).

Application of the advanced oxidation process resulted in an initial increase in THMFP from 402 µg$L^{-1}$ to 465 and 672 µg $L^{-1}$ for doses of 1 and 3 J $cm^{-2}$

respectively (Table 3.2). At 6 J $cm^{-2}$ the THMFP reduced to 265 µg $L^{-1}$ indicating that reduction in NPOC was outweighed by increased reactivity until very large doses were applied. Currently there is a paucity of data on the impact of UV doses above that normally experienced for disinfection especially when followed by chlorination (Dotson *et al*., 2010). However, previous studies have shown no impact at UV doses less than 0.5 J $cm^{-2}$ with 100 mg $L^{-1}$ $H_2O_2$ (Liu *et al*., 2002) suggesting that very different pathways appear at higher UV doses. Kleiser and Frimmel (2000) reported a THMFP increase of 20% after 100 min UV irradiation (15 W) of a river water in presence of 8 mg $L^{-1}$ $H_2O_2$ while a 20% THMFP reduction was observed after 1000 min linked to the point when at least 10% of the DOC had been mineralised. Similarly, limited photocatalysis (≤5 kW h $m^{-3}$) of two surface waters increased THMFP while extended photocatalysis (≥10 kW h $m^{-3}$) achieved significant THM precursor removal (Gerrity *et al*., 2009). Even greater impact has been seen when applying the advanced oxidation process to both post-filtration and post-granular activated carbon water from the Greater Cincinnati Water Works Mille plant which treats Ohio river water with a DOC in the range 2-3 mg $L^{-1}$ (Dotson *et al*., 2010). Application of 1 J $cm^{-2}$ and 10 mg $L^{-1}$ $H_2O_2$ resulted in a doubling of total THM yield. The increase was correlated to a near commensurate increase in chlorine demand attributed to the hydroxylation of native dissolved organic matter (DOM) phenolic structures consistent with the fact that the •OH could target benzene structures resulting in both increased chlorine demand and THM formation (Gallard and von Gunten, 2002).

**Table 3.3 Impact of UV/$H_2O_2$ on bulk parameters and chlorine reactivity**

| Treatment UV/$H_2O_2$ | NPOC (mg $L^{-1}$) | $UV_{254}$ ($m^{-1}$) | SUVA ($m^{-1}$ $mg^{-1}$ L) | THMFP (µg $L^{-1}$) | Specific THMFP (µg $mgC^{-1}$) |
|---|---|---|---|---|---|
| Raw water | 5.3 | 13.3 | 2.5 | 402 | 76 |
| 1 J $cm^{-2}$; 1 mM | 4.9 | 8.1 | 1.6 | 465 | 95 |
| 3 J $cm^{-2}$; 1 mM | 4.1 | 4.7 | 1.1 | 672 | 164 |
| 6 J $cm^{-2}$; 1 mM | 3.9 | 3.2 | 0.8 | 265 | 68 |

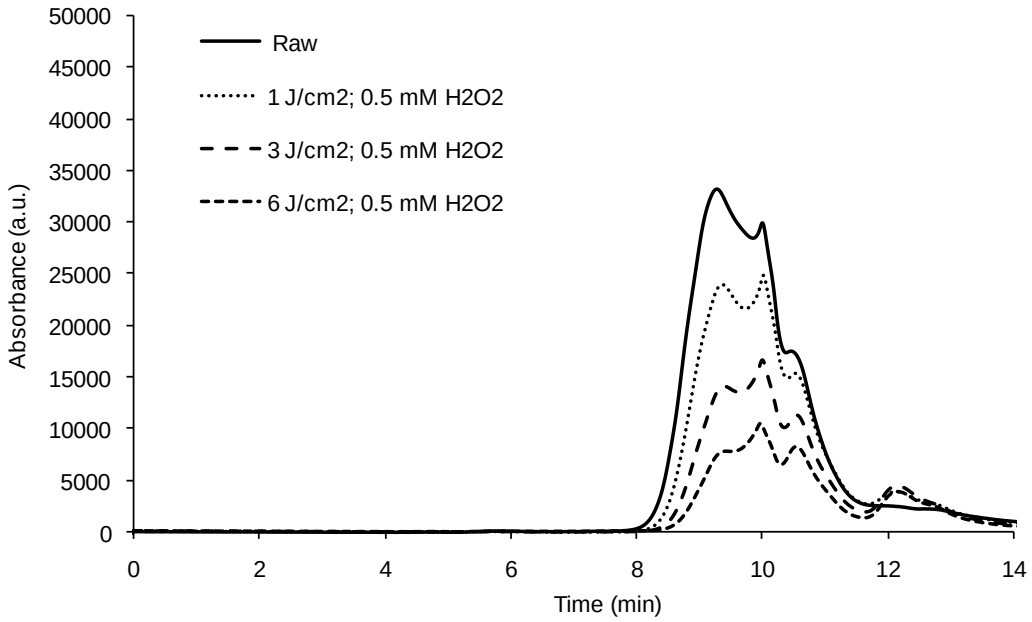
### 3.4.2 The impact of UV/$H_2O_2$ on NOM structure

Investigation into the impact of UV/$H_2O_2$ on the character and structure of NOM in the high alkalinity, highly hydrophilic water currently under investigation revealed a number of specific changes in the character of the water (Figure 3.1). For instance, UV-HPSEC analysis showed that total absorbance generally decreased in accordance with bulk measurements and that the reduction was predominantly observed at shorter elution times, hence larger MW components. For instance, the raw water contained two principle peaks at 9.2 and 10 minutes with corresponding absorbance values of 32500 and 29200 a.u. (Figure 3.1A). Application of 1 J $cm^{-1}$ with 0.5 mM $H_2O_2$ resulted in a decrease in absorbance of 28% and 19% for both peaks respectively such that the second peak become the dominant one suggesting either a preferential reaction between •OH and the larger MW material or partially degraded by-products were adding to the second peak. At higher doses the additional decrease in both peaks was similar suggesting a limiting differential impact as a function of MW consistent with a specific group of components having a higher affinity for •OH rather than just as an overall function of MW. Overall, the application of UV/$H_2O_2$ resulted in a

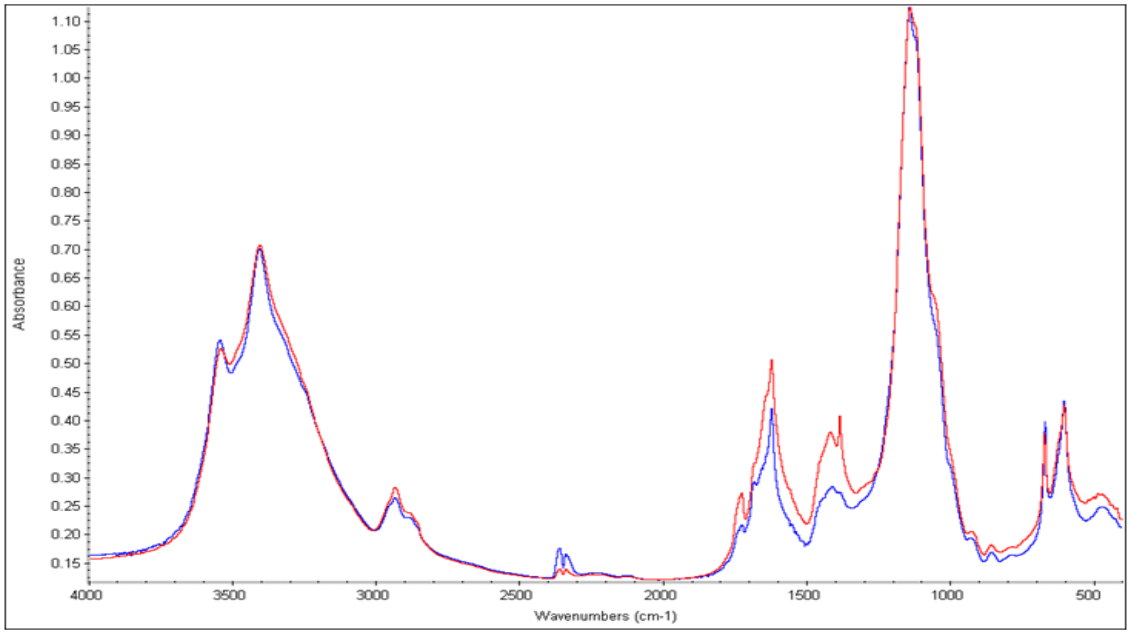
general shift to small MW components as evidence by the proportion of the UV absorbance to the right hand side of the 10 minute elution time (approx 1 kDa) which reduced from a raw water value to 18%, 46% and 67% as the UV dose increased from 1 to 3 and 6 J $cm^{-2}$ respectively. Similar findings have been reported with a low alkalinity reservoir water with a shift toward smaller MW components as progressively higher doses were applied (Sarathy and Mohseni, 2007). Overall this fits with the suggestions by Westerhoff *et al*. (1999) who highlighted a positive correlation between the combination of MW and aromaticity of NOM and the reaction rate constant with hydroxyl radicals.

Further investigation through FTIR spectra revealed the major changes to be associated with increases across the 1720-1700 $cm^{-1}$ (C=O stretching vibration of carboxylic acids and ketones/quinones) and the 1450 $cm^{-1}$ (C-H deformation of aliphatic groups) bands (Figure 3.1B). Linked to the other bands present in both raw and treated samples implies two features: the saturation of compounds (aliphatic compounds) was enhanced and functional groups such as carboxylic acids, aldehydes or ketones were formed. This agrees with previous studies of UV disinfection followed by chlorination which have identified that UV disinfection forms small MW aldehydes, carboxylic acids and general biodegradable compounds (Shaw *et al*., 2000; Linden *et al*., 2004). Similar findings have also been reported during the ozonation of reservoir water and fulvic acid (Chang *et al*., 2002; Li *et al*., 2008) whilst formation of phenols, alcohols and epoxides have also been suggested (Li *et al*., 2008).

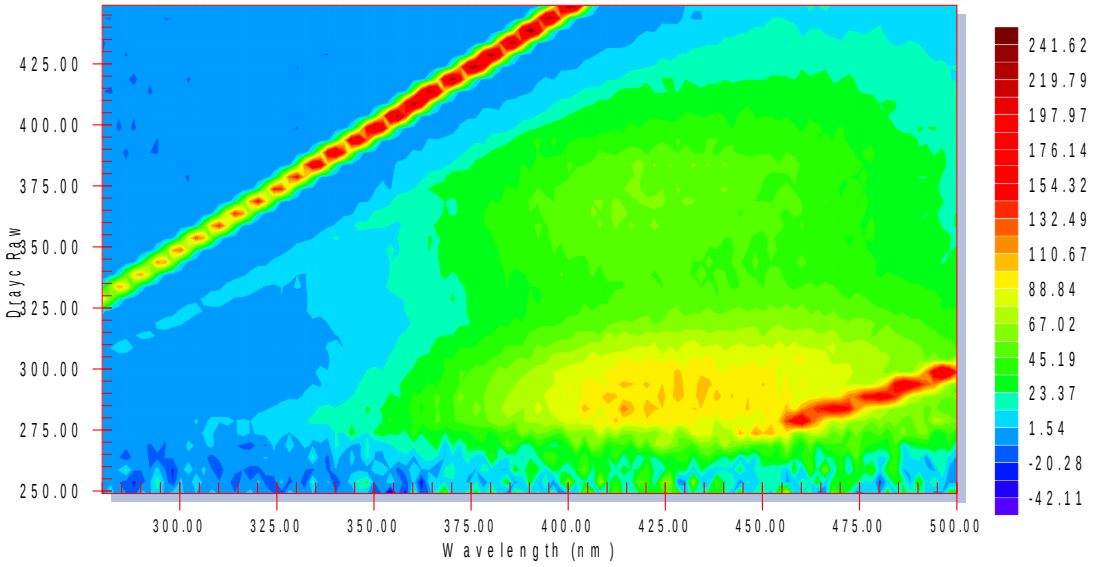
Excitation-emission spectroscopy identified two main peaks at excitation-emission (Ex/Em) bands of 280-290/415-435 [band A] and 360-375/415-425 [band C] (Figure 3.1C) characteristic of humic like material. The relative low intensity in band C compared to band A has previously been interpreted as an indication of the presence of aromatic rings and other unsaturated bond systems (Senesi *et al*, 1991). In addition, the spread of the band centered along 280-290 nm extends in the range of a tryptophan like peak (T1) suggesting the possible influence of some effluent organic matter (EfOM) (Henderson *et al*., 2009). Application of 3 J $cm^{-2}$ and 1 mM $H_2O_2$ (Figure 3.1D) resulted in a reduction of intensity of 73% in peak C (375/425) and 65% in peak A (290/425) which compares to a 65% reduction in $UV_{254}$ and a 23% in NPOC (Table 3.2). Overall, this indicates that the characteristics of the organic material have changed with the observed change towards smaller MW components likely to contain an increase in functional groups such as carboxylic acids, aldehydes and ketones( Shaw *et al*., 2000; Linden *et al*., 2004).



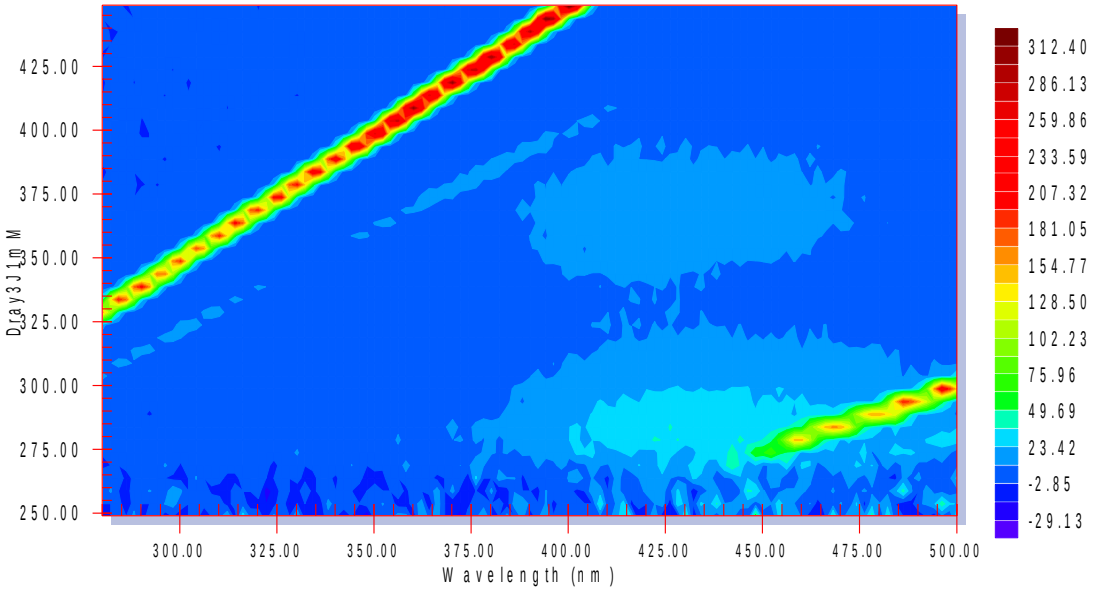

(A) HPSEC chromatogram




(B) FTIR spectra from raw water (blue), UV/$H_2O_2$ treated water at 3 J $cm^{-2}$ and 1 mM (red)




(C) Fluorescence EEM spectra of raw water



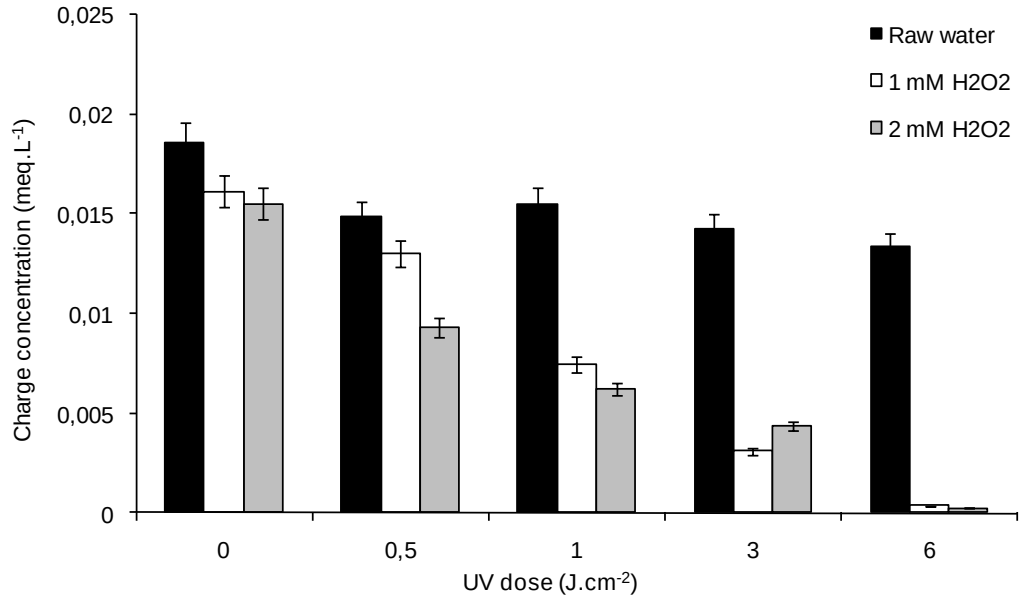

(D) Fluorescence EEM spectra of UV/$H_2O_2$ treated water at 3 J $cm^{-2}$ and 1 mM $H_2O_2$

**Figure 3.4 Characterisation for raw water and after UV/$H_2O_2$ treatments at 1; 3 and 6 J $cm^{-2}$ and 0.5 mM $H_2O_2$.**

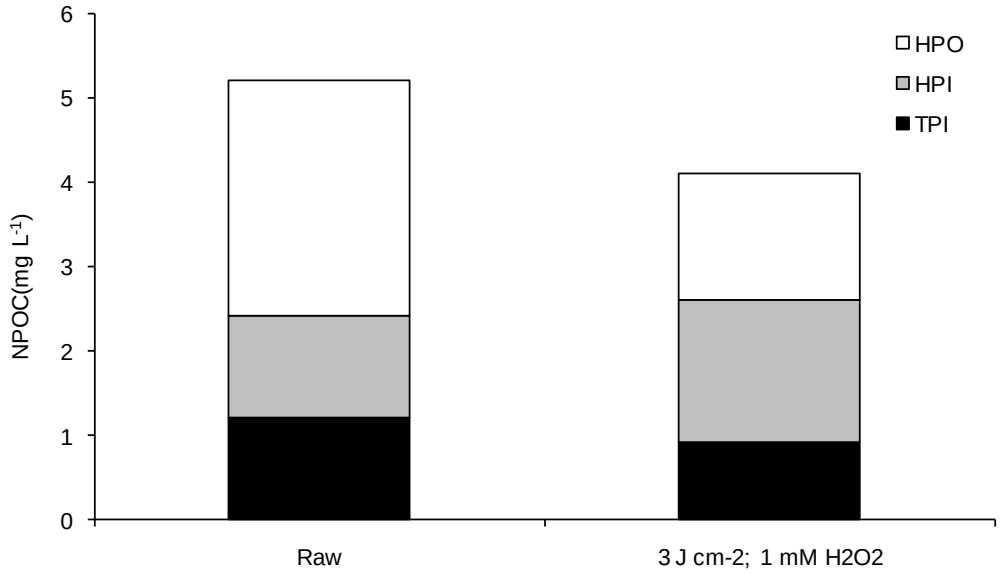
In order to relate changes in organic character to treatment both charge density and hydrophobicity were monitored as they have been shown to directly relate to both coagulation and adsorption processes (Sharp *et al*., 2006a; Pidou *et al*., 2008; Bond *et al*., 2010). The raw water exhibited a charge concentration at 0.018 meq $L^{-1}$ equivalent to a charge density of 3.4 meq $g_{DOC}^{-1}$ (Figure 3.2A) which is similar to previously reported values for natural organic matter using a similar measurement technique at between 3.6-5.1 meq.$g_{DOC}^{-1}$ (Sharp *et al*., 2006). Direct photolysis of the water with UV doses between 0.5-6 J $cm^{-2}$ caused a slight decrease in charge concentration to between 0.014-0.015 meq $L^{-1}$ which represents a maximum decrease of 22%. In contrast, oxidation of the organic material by UV/$H_2O_2$ resulted in a dramatic decrease in charge such that at a UV dose of 6 J $cm^{-2}$ the water exhibited negligible charge. Corresponding reduction in charge concentration at UV doses of 0.5, 1 and 3 J $cm^{-2}$ [1 mM $H_2O_2$] were 0.013, 0.0075 and 0.0043 meq $L^{-1}$ indicating a progressive reduction in charged components in the water with increasing UV dose. Taking into account the corresponding reduction in NPOC the respective charge density of the water after advanced oxidation process treatment was 2.6, 1.8 and 1.1 meq $g_{DOC}^{-1}$. Comparison between the two reveals that the charge concentration is reduced more significantly than the charge density of the organic material reflecting the general recalcitrance of the NPOC to advanced oxidation process treatment. The charge density levels observed after advanced oxidation process are similar to those reported for other types of organics with levels of 0.6-2.4 meq $g_{DOC}^{-1}$ for greywater (Pidou *et al*., 2008) and 0.1-3.2 meq $g_{DOC}^{-1}$ for algal organic matter (Henderson *et al*., 2006). In both

cases the reduced charge character of the organic matter has been linked to a reduced efficiency of coagulation (Henderson *et al*., 2010).

Consideration of the aromaticity in terms of SUVA suggests the water is a mix of hydrophobic and hydrophilic material with a raw water value of 2.5 $m^{-1}$ $mg^{-1}$ L. Fractionation with XAD resins confirmed this with 48% of the recovered NPOC being attributed to the hydrophilic fractions (Figure 3.2B). Oxidation of NOM resulted in an increase in the hydrophilic material from 1.2 to 1.7 mg $L^{-1}$ and a reduction in the hydrophobic content from 2.8 mg $L^{-1}$ to 1.5 mg $L^{-1}$ indicating that the oxidation process principally acted on the hydrophobic components. Such a suggestion is consistent with the view that the AOP results in hydroxylation of native DOM phenolic structures (Dotson *et al*., 2010) and is similar to previous findings related to the application of ozone (Bose and Reckhow, 2007). However, other researchers have shown a conversion of hydrophobic to hydrophilic material as a result if advanced oxidation process treatment. For example, Sarathy and Mohseni (2009) reported the conversion of 25% of hydrophobic NOM to hydrophilic NOM after a UV dose of 1.5 J $cm^{-2}$ and 20 mg $L^{-1}$ (0.59 mM) of $H_2O_2$. Overall, analysis of the water indicates a reduction in both hydrophobic content and charge associated with the organic matter resulting in a water containing organic matter principally characterised as uncharged and hydrophilic and thus similar to the characteristics of algal organic matter (Henderson *et al*., 2006), grey water (Pidou *et al*., 2008) or effluent organic matter.




(A)




(B)

**Figure 3.5 Charge concentration of UV/$H_2O_2$ treated water (0-6 J cm$^{-2}$ and 0-2 mM $H_2O_2$) (A) and fractionation of raw and treated water (3 J.cm$^{-2}$, 1 mM $H_2O_2$) (B)**

### 3.4.3 Impact of UV/$H_2O_2$ on traditional treatments

#### *3.4.3.1 Impact of UV/$H_2O_2$ on coagulation*

Coagulation of the raw water under acidic conditions (pH 4.5) resulted in a decrease in the NPOC from 3.8 mg $L^{-1}$ to 1.75 mg $L^{-1}$ as the coagulant dose (no advanced oxidation process) was increased from 0 to 10 $mg_{Fe}.L^{-1}$ (Figure 3.3B) representing a maximum NPOC removal of 54%. Comparison with the fractionation data indicates that at the higher doses the residual NPOC was approaching the value of the raw water hydrophilic component which is known to be recalcitrant to coagulation (Sharp *et al*., 2006a) and as such coagulation was optimized at ferric doses of around 7 $mg_{Fe}$ $L^{-1}$. However, the majority of NPOC removal was achieved with a dose of 3 $mg_{Fe}$ $L^{-1}$ which resulted in a residual NPOC of 2.2 mg $L^{-1}$. Removal was more pronounced in terms of $UV_{254}$ as indicated by the fact that doses of 2, 3, 5 $mg_{Fe}$ $L^{-1}$ resulted in a decrease in $UV_{254}$ from a raw water value of 0.13 $cm^{-1}$ to 0.06, 0.05 and 0.045 $cm^{-1}$ respectively (Figure 3.3A). Maximum removal was again seen at the maximum dose tested at a level of 72% demonstrating preferential removal of $UV_{254}$ absorbing compounds during the coagulation process. Pretreatment of the water with 3 J $cm^{-1}$ and either 1 or 2 mM $H_2O_2$ resulted in no significant difference in the residual NPOC or $UV_{254}$ upon coagulation compared to the addition of coagulant alone. An exception to this was observed in relation to $UV_{254}$ at low coagulant doses where pretreatment with the advanced oxidation process generated lower residual $UV_{254}$ values (Figure 3.3A). However, the improved performance was observed pre- coagulation indicating that the

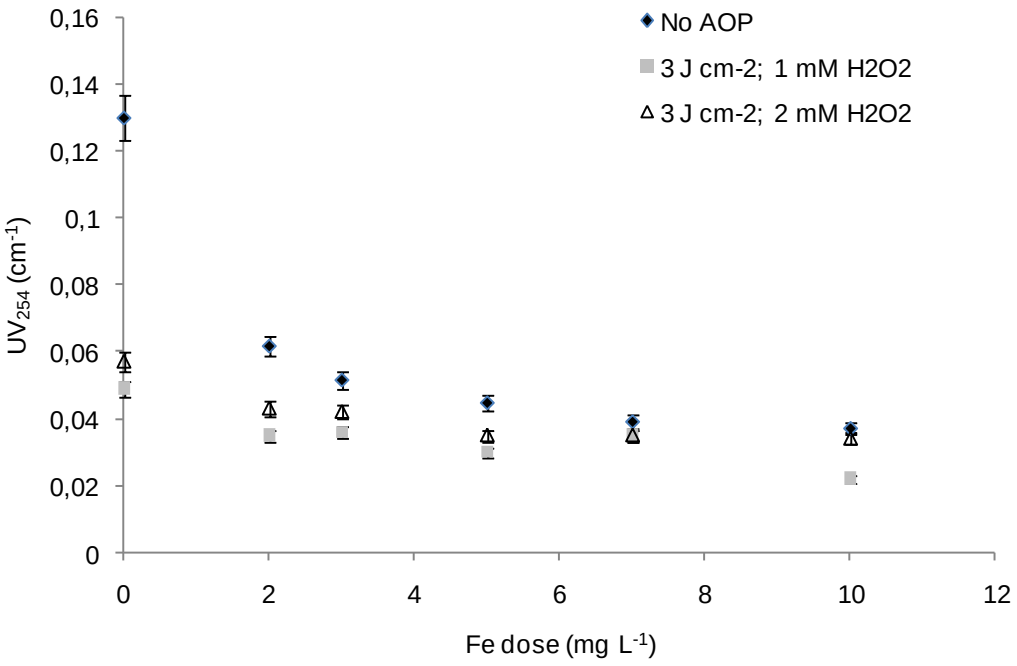
removal had occurred during the advanced oxidation process. In fact, no further removal of $UV_{254}$ was apparent during coagulation suggesting that the two processes were interacting with the same components in the water.

The same overall observation that pretreatment with UV/$H_2O_2$ did not enhance coagulation was also apparent at pH 7.6, a more realistic pH condition for the target water. Again no difference in NPOC residual could be observed between coagulation with and without advanced oxidation process pretreatment across coagulant doses of 2-10 $mg_{Fe}$ $L^{-1}$ (Figure 3.3D). Residual NPOC level varied between 2.3-3.5 mg $L^{-1}$ for doses of 2-7 $mg_{Fe}$ $L^{-1}$ but decreased to 2.6 mg $L^{-1}$ at the highest doses tested. Consequently the residual NPOC was roughly 1 mg $L^{-1}$ higher at pH 7.6 compared to pH 4.5 for both the coagulation and the advanced oxidation process + coagulation cases. A similar situation was observed in terms of $UV_{254}$ with regards to the advanced oxidation process pretreatment cases where higher residual values were observed when operated at pH 7.6. To illustrate, in the case of the 2 mM $H_2O_2$ case minimum residuals of 0.034 $cm^{-1}$ and 0.045 $cm^{-1}$ were observed at pH 4.5 and 7.6 respectively representing corresponding removal levels of 74% and 65%. However, there was a marked difference when compared to coagulation without AOP pretreatment where $UV_{254}$ decreased to a minimum residual of 0.078 $cm^{-1}$ (40%) at the maximum coagulant dose (Figure 3.3C). Consequently, the advanced oxidation process enabled an additional 0.033 $cm^{-1}$ $UV_{254}$ to be removed which represents an extra 25% removal although this was purely as a direct result of the advanced oxidation process and not a conditioning effect that enabled improved coagulation. The current findings support previous studies

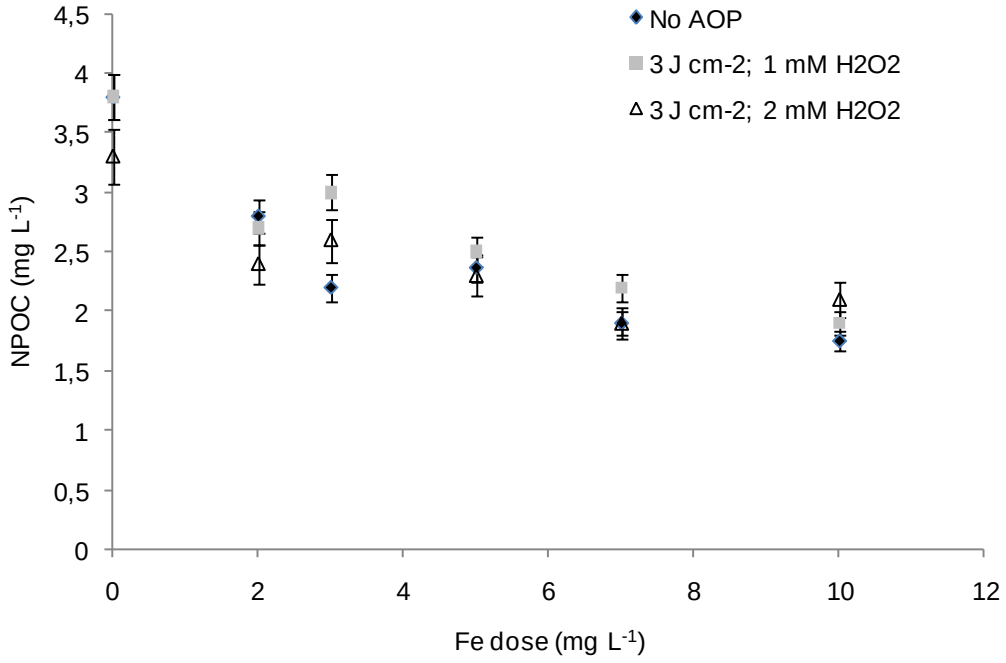
with ozone which showed improved removal of $UV_{254}$ from 57% to 75% with a dose of 0.5 $mgO_3$ per mgC (Teksoy *et al*., 2008) but not the decreased removal of DOC reported by Liu *et al*. (2006).

The coagulation process is known to be driven by a combination of charge and adsorptive pathways that results in the formation of organo-metal complexes and/or organo-MeOH complexes (Sharp *et al*., 2006b; Henderson *et al*., 2006; Henderson *et al*., 2010). The high alkalinity and pH of the water during coagulation results in the latter generally being considered the more important and is typically referred to as sweep flocculation whereby iron hydroxide nanoparticles initially form which then act as adsorption sites for the removal of dissolved organics. The fundamental mechanisms which operate during sweep flocculation remain poorly understood (Bache *et al*., 1999; Duan and Gregory, 2003) although it is agreed that the resultant organic-hydroxide particles can only combine if the net charge of the coated particles is sufficiently low. Consequently, coagulation is known to be most effective in removing charged hydrophobic material (Sharp *et al*., 2006a; Bond *et al*., 2010). Viewed in terms of the above, the observed results are consistent with the changes in characterization of the organic material as a reduction in charge and hydrophobicity has been observed. This is in agreement with Li *et al*. (2009) who highlighted that the formation of lower MW and higher hydrophilic ozonation by-products reduced coagulation performance. Further, Bose and Reckhow (2007) demonstrated that ozone reacted preferentially with the hydrophobic fraction of NOM resulting in the detrimental effects of ozonation on subsequent NOM removal by coagulation. This was ascribed as a decline in

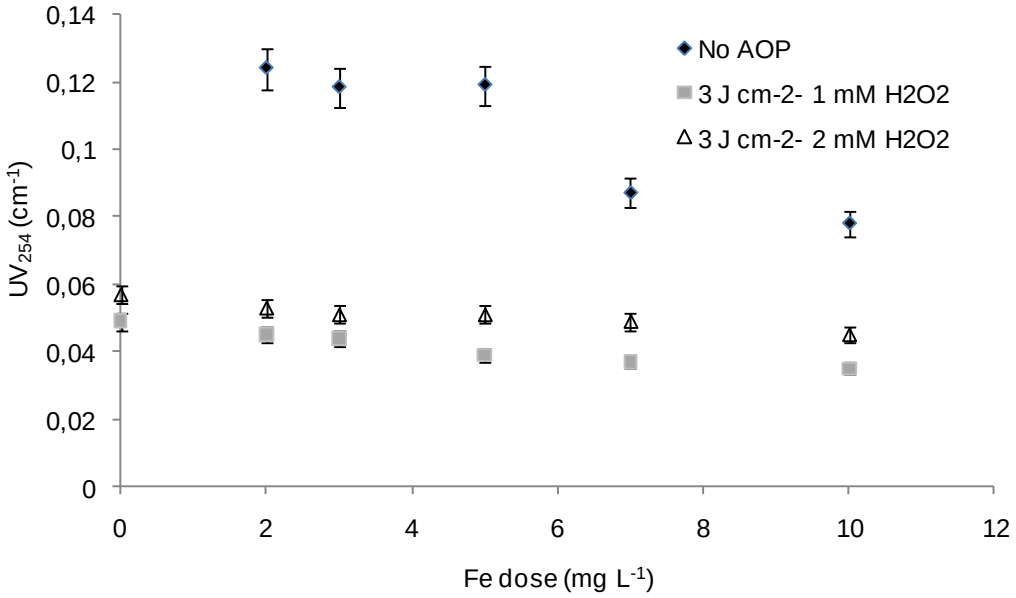
adsorption affinity of the hydrophobic fraction to the floc surface. Overall, the advanced oxidation process appears to be affecting similar components to the coagulation process and to form by-products that have a negligible affinity for removal by coagulation. This is confirmed by the fact that similar experiments conducted with the advanced oxidation process utilized post-coagulation [Scheme C] did not generate any significant differences in net removal (data not shown). One exception to this overall picture is in the case of the $UV_{254}$ absorbing components at higher pHs where the advanced oxidation process appears to have a greater affinity than the coagulation process reflecting the differences in their reaction pathways.



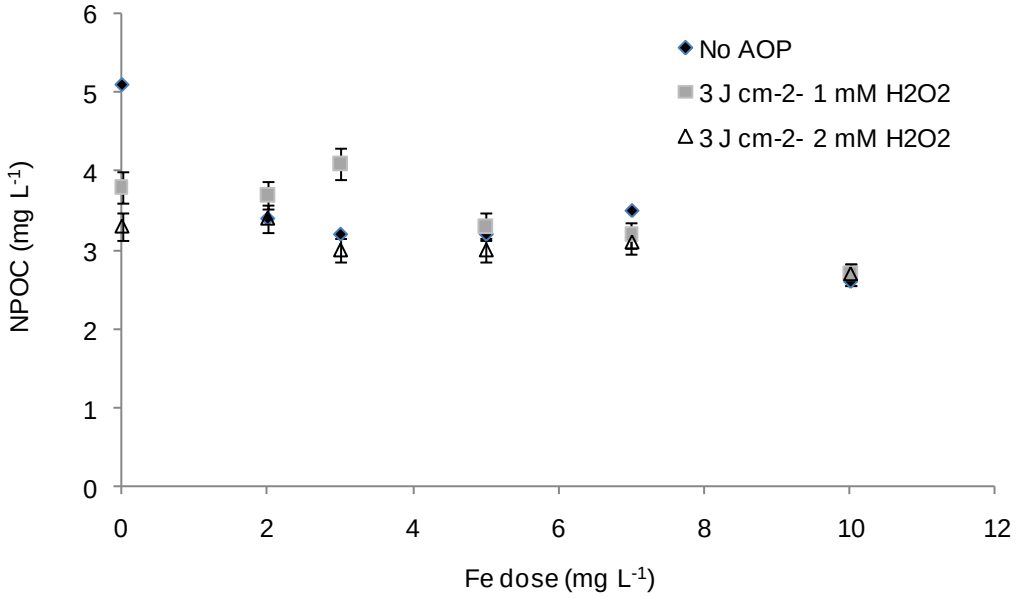

(A). $UV_{254}$ removal after UV/$H_2O_2$ and coagulation at pH 4.5




(B). NPOC removal after UV/$H_2O_2$ and coagulation at pH 4.5




(C) $UV_{254}$ removal after UV/$H_2O_2$ and coagulation at pH 7.6




(D) NPOC removal after UV/$H_2O_2$ and coagulation at pH 7.6

**Figure 3.6 Impact of UV/$H_2O_2$ (3 J $cm^{-2}$ and 1-2 mM $H_2O_2$) and coagulation (0-10 mg $L^{-1}$ as Fe and pH 4.5 and 7.6) on NOM removal**

### *3.4.3.2 Impact of UV/$H_2O_2$ on GAC*

Equilibrium adsorption analysis of the raw and coagulated water post-treated with an advanced oxidation process revealed the most appropriate isotherm model to be the modified Freundlich isotherm model (Figure 3.4). Analysis of the isotherms in terms of the Freundlich capacity indicates that the oxidation of the organics post-coagulation increased the capacity of the GAC from 4.77 $mg_C$ $g_{GAC}^{-1}$ post-coagulation to 9.75 $mg_C$ $g_{GAC}^{-1}$ post-coagulation+UV/$H_2O_2$ (1 min RT) although this decreased to 6.12 $mg_C.g_{GAC}^{-1}$ when coagulation+UV/$H_2O_2$ (3 min RT) were applied (Table 3.3). All three waters exhibited a lower capacity than the raw water at 10.8 $mg_C$ $g_{GAC}^{-1}$. At a target residual concentration of 1 mg $L^{-1}$ DOC the capacity of the GAC was 11; 9.5; 5.7 and 4.5 $mg_C$ $g_{GAC}^{-1}$ for the

raw water, coagulation+1minRT, coagulation+3 min RT and coagulated water respectively.

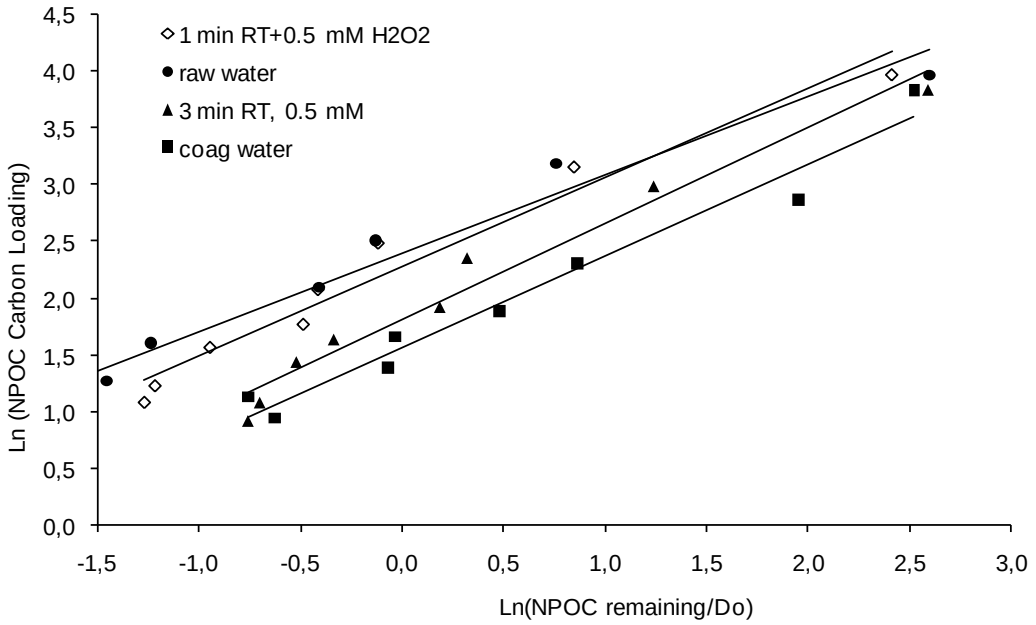



**Figure 3.7.Modified Freundlich isotherms after UV/$H_2O_2$ treatment (1-3 min RT and 0.5 mM $H_2O_2$)**

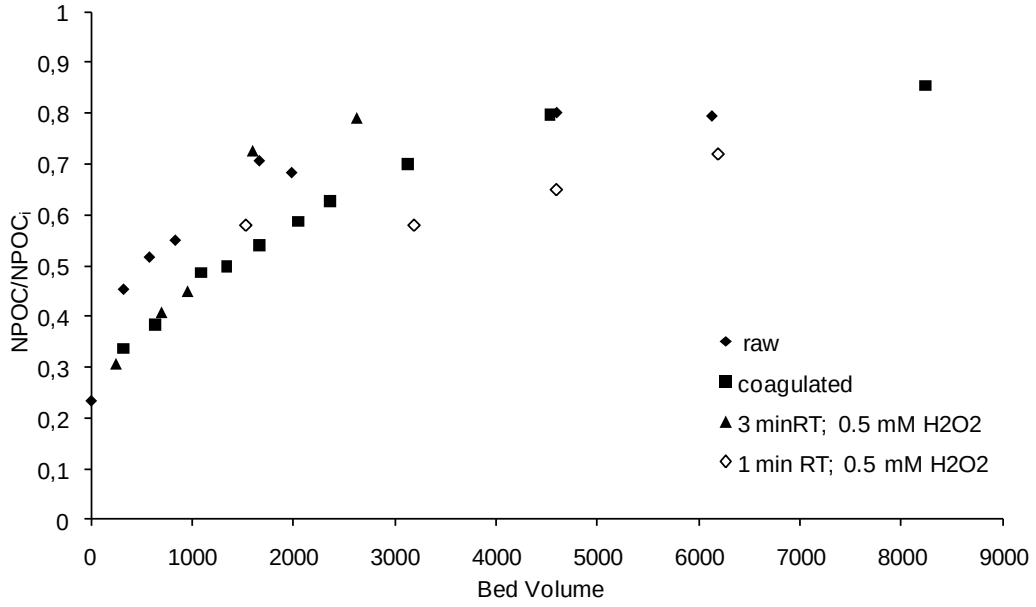
**Table 3.4 Modified Freundlich parameters**

| Treatment | Kf | 1/n | $R^2$ |
|---|---|---|---|
| Raw water | 10.80 | 0.69 | 0.96 |
| Coagulated water | 4.77 | 0.80 | 0.97 |
| Coag.+ UV/$H_2O_2$ (1 min RT; 0.5 mM) | 9.75 | 0.78 | 0.96 |
| Coag.+ UV/$H_2O_2$ ( 3 min RT; 0.5 mM) | 6.12 | 0.84 | 0.97 |

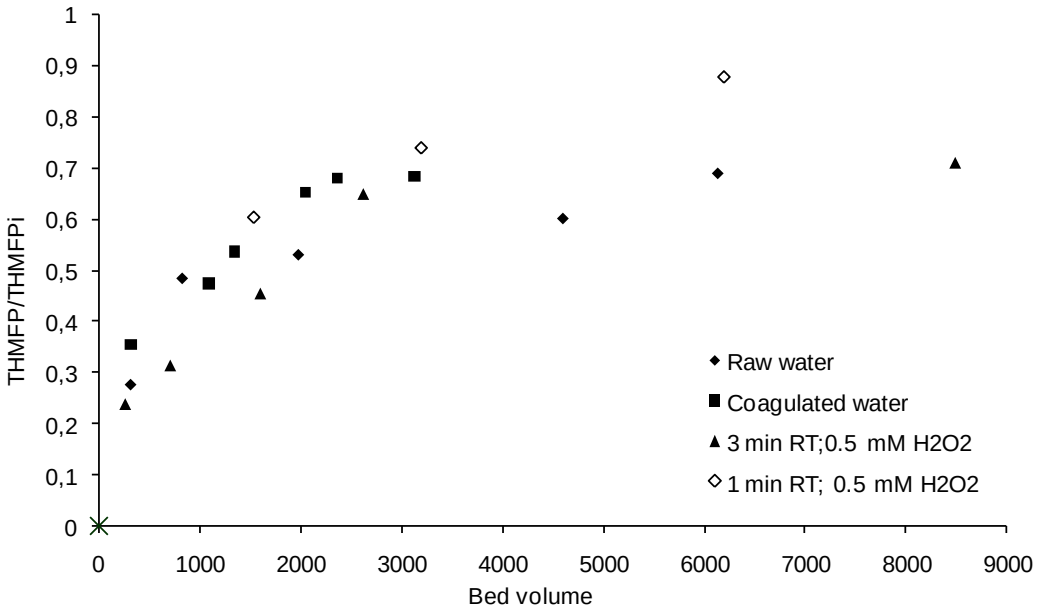
Kinetic experiments based on a RSSCT system revealed similar removal profiles for the first 1700 bed volumes (BV) beyond which each treatment exhibited a different response. The presence of an initial breakthrough (at BV = 0) suggests either a limited affinity of the organics for the GAC or that hydraulics performances of the column should be optimized. Alternatively, In the case of the coagulated water, the removal was enhanced over that of the raw water up to 4200 BV beyond which the carbon reached saturation at around 22 % removal of the NPOC (Figure 3.5A). Inclusion of a post-coagulation oxidation stage with 1 J $cm^{-2}$ and 0.5 mM $H_2O_2$ resulted in improved removal across the GAC column with an increase in NPOC removal from 20 to 40% observed between 3000 and 6000 BV. In contrast, application of a higher UV dose of 3 J $cm^{-2}$ decreased adsorption with the column reaching near capacity at 2400 BV indicating the impacts of the advanced oxidation process is relatively subtle in terms of the by-products formed. Residual $H_2O_2$ after UV/$H_2O_2$ treatment should also be considered as it is a cytotoxic bacterial mutagen which interferes with disinfection processes by reaction with chlorine. It is worth noting that no significant residual $H_2O_2$ was found at the effluent of the GAC columns using 17 mg $L^{-1}$ as $H_2O_2$ initial concentration and 1 to 6 min treatment. This is consistent

with Kamp *et al*. (2007) who reported that GAC effectively removed residual $H_2O_2$ at full scale when 6 mg $L^{-1}$ was used as initial concentration. Conversion of the data into THM precursor removal, by measuring the THMFP of the residual organic matter, revealed a different picture to that of NPOC (Figure 3.5B). In terms of THMFP, the higher UV dose had the most beneficial impact with a plateau removal of 40% THMFP achieved after 3000 BV which was similar to that for the raw water. In comparison, coagulation alone and coagulation with a lower dose of advanced oxidation process (1 J $cm^{-2}$, 0.5 mM $H_2O_2$) provided only a 28% removal at 3000 BV which then further declined as the run continued. In total ~17 % more THMFP precursor material was removed with the higher UV dose reflecting the generation of simpler chemical structures (Bond *et al*., 2009a). The observations made from the current study on high alkalinity, highly hydrophilic waters are consistent with studies on fulvic acid where a 20% DOC decrease in adsorption was reported after ozonation (Kim *et al.*, 1997). Similarly, Chang *et al*. (2002) linked a reduction in removal of model compounds (humic acid, p-hydroxybenzoic acid and hydroquinone) by ozone/GAC to an increase in polarity of the by-products. Previous studies with model compounds support this suggestion where hydrophobic components typified by phenolics such as ferulic acid and resorcinol have $\log K_{OW}$ of around 0.8-1.5 compared to typical hydrophilic/transphilic components such as carboxylic acid (oxalic acid, 3-oxopentanedioic acid) and amino acid ($_L$-tryptophan, $_L$-leucine) compounds with $\log K_{OW}$ of -0.19 to -1.13 and -1.06 to -1.52 respectively (Bond *et al*., 2009b). The impact of hydrophobicity has also been demonstrated through preferential removal of the hydrophobic

components in real waters (Schreiber *et al*., 2005). However, this does not necessarily reflect a reduction in THM formation as there is no strong correlation between hydrophobicity and DBP formation with structural rather than physicochemical parameters controlling DBP formation potential (Bond *et al.*, 2009b). Overall, the impact of the advanced oxidation process post-coagulation appears very sensitive to applied dose. The difference between 1 and 3 min RT suggests the type of by-products formed is of importance with lower UV doses forming by-products more amenable to adsorption than either the pre-oxidized material or the more heavily oxidized material and higher UV doses forming precursors that form less THMs. This may indicate the lower doses tend to form carboxylic acid functional groups more readily adsorbed than aldehydes and ketones as the former tend to be more hydrophobic.




(A).




(B).

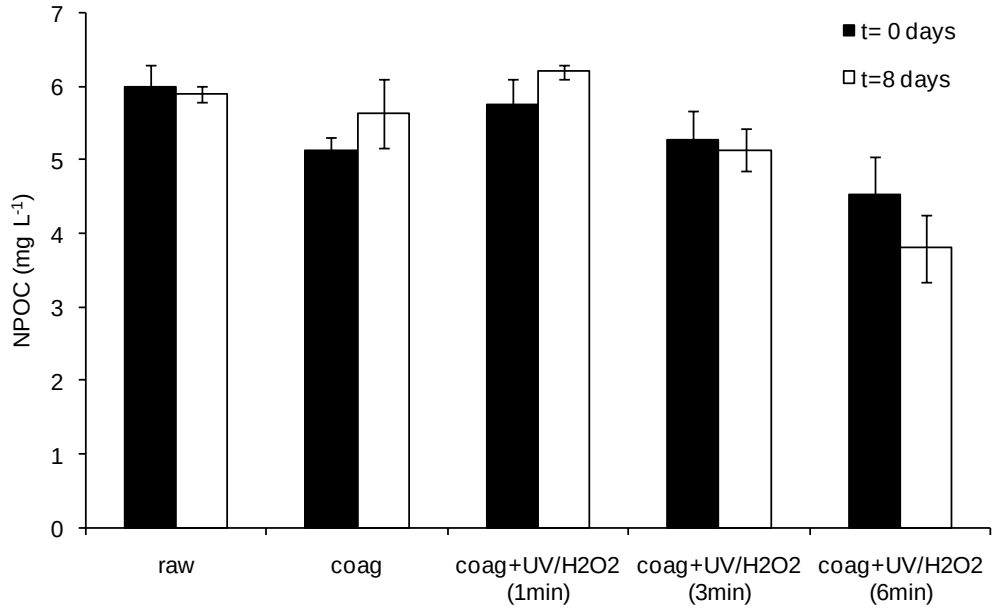
**Figure 3.8 NPOC (A) and THMFP (B) breakthrough curves for raw, coagulated and pre-coagulated UV/$H_2O_2$ treated waters (1-3 min RT and 0.5 mM initial $H_2O_2$ dose).**

### *3.4.3.3 Impact of UV/$H_2O_2$ on biotreatment*

Assessment on the impact of advanced oxidation processes on the efficiency of downstream biotreatment revealed a limited influence as measured in a BDOC batch test (Figure 3.6A). The raw water did not exhibit any significant BDOC content suggesting any biotreatment would be driven from the production of biodegradable by-products formed during the advanced oxidation process stage. NPOC was reduced in the case of the 6 min RT advanced oxidation process from a raw water NPOC of 6 mg $L^{-1}$ to 4.6 mg $L^{-1}$ after coagulation+6 min RT, 0.5 mM $H_2O_2$ and 3.8 mg $l^{-1}$ after subsequent biotreatment. Consequently, NPOC removals of 23% and 37% were observed for coag+AOP and coag+AOP+biotreatment respectively indicating active biotreatment. In all other cases no significant difference after biotreatment could be observed with some instances of an increase in NPOC, presumably a consequence of the production of soluble microbial products. Similar results were reported by Yavich *et al*. (2004) who studied the biodegradability of a raw water which was refractory to biodegradation and did not exhibit any further change in BDOC after preozonation at 1.5 mg $O_3$ per mgC. In contrast, Buchanan *et al*. (2004) reported a significant increase in biodegradability of 23-40% after UV and vacuum UV (VUV) treatment using 25-250 J $cm^{-2}$ corresponding to 30-180 min RT. Consequently, it appears very high doses are required to drive the by-products formation towards compounds that exhibit enhanced biodegradability which seems to be starting to occur at the highest dose tested in the current investigation.

In contrast, biotreatment of the raw water resulted in a significant reduction in THMFP from 135 to 90 µg.$L^{-1}$ (Figure 3.6B). Biotreatment of coagulated and coagulation+ UV/$H_2O_2$ did not alter the THMFP which remained between 80-90 µg.$L^{-1}$ in all cases except the application of 3 min RT, 0.5 mM $H_2O_2$ prior to biotreatment which showed an increase to 121 µg.$L^{-1}$. Subsequent biotreatment returned the THMFP to a level consistent with the other systems tested.

THMFP results did not reveal any significant benefits of UV/$H_2O_2$ pretreatment on the biodegradability. However it could be noted that after 3 min irradiation and 0.5 mM $H_2O_2$ the THMFP content increased significantly from 84 to 121 µg $L^{-1}$ and subsequently dropped back to the initial level (84 µg $L^{-1}$) after 8 days of contact with the bioactive sand. The lack of a change in THMFP after batch BDOC test in the current study contrasts with those reported using AOP coupled with biological activated carbon (BAC) columns. For example, substantial NPOC and THMFP removals of 52% and 42% respectively were reported after UV/$H_2O_2$ treatment of a low alkalinity, low DOC raw surface water at 0.5 J $cm^{-2}$ and 20 mg $L^{-1}$ $H_2O_2$ (Toor and Mohseni, 2007). The effectiveness of the BAC was reported to depend on both the characteristics of the NOM and of the activated carbon as well as the type and extent of oxidative pretreatment (Gauden *et al*., 2006).

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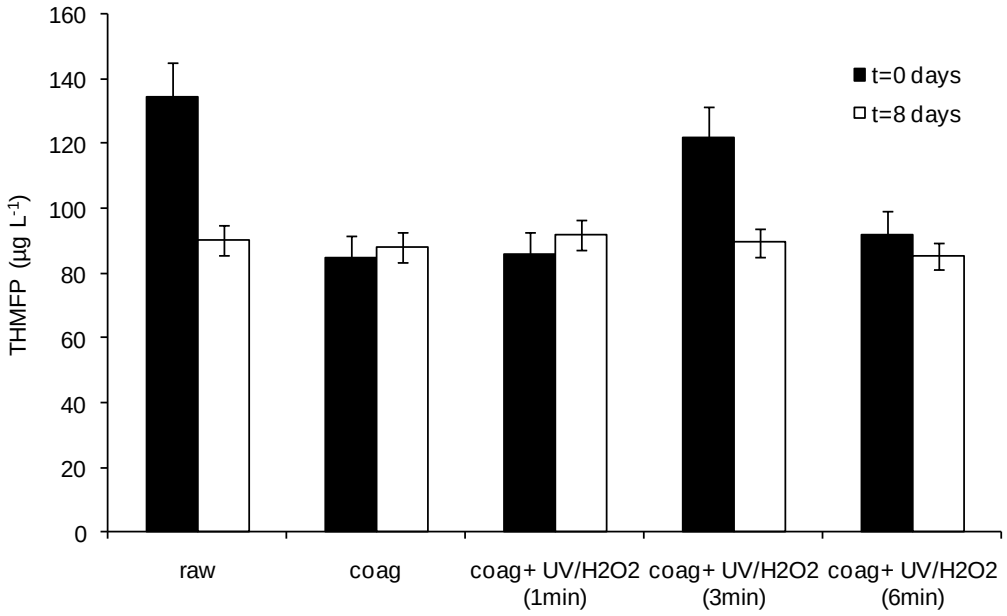


(B)

**Figure 3.9 Impact of coagulation, UV/$H_2O_2$ and biotreatment on NPOC (A) and THMFP (B) removal**

## 3.5 Conclusions

The UV/$H_2O_2$ treatment of a high alkalinity and hydrophilic rich reservoir water revealed moderate NPOC removal at UV doses up to 6 J $cm^{-2}$ and 2 mM $H_2O_2$. However, significant structural changes of the NOM were highlighted: loss of aromaticity and conjugated double bonded species, shift towards lower molecular weight species, formation of oxygenated by-products such as carboxylic acids and ketones/quinones. Consequently, reactivity towards chlorine was enhanced at doses ≤3 J $cm^{-2}$ and reduced at higher UV doses. Linking UV/$H_2O_2$ to standard water treatment processes such as coagulation, GAC and biotreatment showed a generally limited benefit or reduction in performance linked to the change in character of the organics. GAC columns tests revealed moderate benefits in terms NPOC and THMFP capacity and enhanced biotreatment at very high UV doses. Overall the study suggests that the application of advanced oxidation processes with high alkalinity, highly hydrophilic waters needs careful consideration and that more information is required in relation to the link between applied dose and by-product formation so that tailored solutions can be developed.

## 3.6 Acknowledgements

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# 4 Photocatalytic oxidation, GAC and biotreatment combinations: an alternative to the coagulation of hydrophilic rich waters?

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## 4.1 Abstract

This study investigated the photocatalytic oxidation of a high alkalinity raw water rich in hydrophilic natural organic matter (NOM) and the impact on non purgeable organic carbon (NPOC), UV absorbance at 254 nm ($UV_{254}$) and trihalomethanes formation potential (THMFP) removals. NPOC and $UV_{254}$ removals were 40% and 55% respectively after 1 min irradiation time and 1 g $L^{-1}$ as $TiO_2$. THMFP content was reduced from 305 µg $L^{-1}$ in raw water to 144 µg $L^{-1}$ after 10 min treatment while chlorine reactivity was stable with treatment. Results showed that larger MW species were preferentially degraded during the process. NPOC and THMFP removals reached 60% and 70% respectively after photocatalytic oxidation and granular activated carbon (GAC) columns.

## 4.2 Introduction

Chemicals are widely used in the water industry and are critical to both the successful production of potable water and the treatment of wastewater. Water utilities have been experiencing both chemical price increases and chemical shortages in recent years and this has potential implications for regulatory compliance, environmental health and sustainability. Total chemical usage by the water utilities in the UK is ~685k metric tonnes per year with chemicals such as lime and coagulants like alum, ferrous and ferric salts making up the most widely used on a mass basis (Henderson *et al*., 2009). This chemical use equates to around 0.07 tonnes of chemical per million litres of potable water supplied and a similar figure per million litres of wastewater treated. Of these chemicals, only 0.1% is reused or recycled. Overall chemical costs account for approximately 10% of the operating costs for water and wastewater treatment and whilst this might not sound a significant figure increasing cost and dwindling availability of chemicals means that reducing, replacing or recycling chemicals is firmly on the research agenda (Hardy, 2007). Among chemical costs, coagulant costs have increased up to 33% but availability is a bigger challenge. This is because the source of many of the coagulants is a by-product from other processes and manufacturing industries which are now dwindling in the global recession, such as steel or titanium production (Henderson et al., 2009).

The removal of natural organic matter (NOM) is important as the reactions with chlorine-based disinfectants lead to the formation of halogenated by-products (Goslan *et al*., 2009), the most prevalent being trihalomethanes (THMs) and

haloacetic acids (HAAs). For waters that are rich in NOM, coagulants such as aluminium and iron play a key role in removing the organic levels (Jarvis *et al*., 2008). There has been recent interest in alternatives to the coagulation process such advanced oxidation processes (AOP) (Comninellis *et al*., 2008). One promising advanced oxidation process is photocatalytic oxidation as it does not require any additional chemicals or pH adjustment and no sludge is formed during the process (Murray and Parsons, 2004). To date a number of studies have shown the potential of photocatalytic oxidation as an organic removal process for drinking water treatment. Han *et al.* (2006) for example reported 30% and 90% dissolved organic carbon (DOC) and $UV_{254}$ removal from a solution of commercial humic acid when using 2 g $L^{-1}$ $TiO_2$ in a rotating photoreactor (UVA, 15 W) after 120 minutes irradiation.

A well known challenge of using a slurry photocatalytic oxidation process is how to separate the catalyst. Gerrity *et al.* (2009) reported performance data for commercial photocatalytic oxidation process on two different raw waters (DOC content of 4.8-7.4 mg $L^{-1}$, $UV_{254}$ of 4.6-11 $m^{-1}$, pH 7.7-8.5 and alkalinity of 105-160 mg $L^{-1}$). Two energy ranges were tested: ≤ 5 kW h $m^{-3}$ and ≤ 320 kW h $m^{-3}$. Limited photocatalysis (≤ 5 kW h $m^{-3}$) led to an increase in THM formation potential (THMFP) from 80 µg $L^{-1}$ up to 140 µg $L^{-1}$ indicating the formation of more reactive organics which would most likely need downstream treatment before contacting with chlorine. Conversely, extended photocatalysis (up to 320 kW h $m^{-3}$) reduced the THMFP by 95% while coagulation at pH 5.5-7 and 20-60 mg $L^{-1}$ as $FeCl_3$ achieved 20-30% THMFP reduction.

Few studies have examined the combination of photocatalytic oxidation and downstream processes. Here we have investigated the use of the photocatalytic oxidation as an alternative to coagulation for a raw water best described as being high in alkalinity and rich in hydrophilic natural organic matter. Degradation of NOM was monitored by DOC, $UV_{254}$, molecular weight distribution (HPSEC) and THMFP at various irradiation times. We have also investigated the use of granular activated carbon (GAC) and biotreatment as a downstream processes to see if they are effective in removing the oxidation products. UV-C and vacuum UV (VUV) irradiation of NOM was reported to form low molecular weight carbonyl by-products such as formaldehyde, acetaldehyde, glyoxal and glyoxylic acid which were effectively removed after biotreatment (Thomson *et al*., 2002, 2004). Ozonation followed by biotreatment has been reported to be effective at controlling DBPs formation . For example, ozonation of a lake water at 3 mg $O_3$ per $mg_{TOC}$ resulted in 10% THMFP removal while 40% THMFP removal was reported when ozonation was followed by biotreatment (Speitel *et al*., 1993).

## 4.3 Materials and Methods

### 4.3.1 Water characteristics

Raw water was collected from a water treatment works in Severn Trent Water region. The water had a non purgeable organic carbon (NPOC) content of 6.8 mg $L^{-1}$, $UV_{254}$ of 14 $m^{-1}$, pH 7.9 and alkalinity of 180 mg $L^{-1}$. The SUVA value of

2 L $mg^{-1}$ $m^{-1}$, which is the ratio of the $UV_{254}$ (in $m^{-1}$) by the DOC (in mg $L^{-1}$), suggests that the studied water consists of a mixture of humic material and other NOM having hydrophobic and hydrophilic character respectively (Goslan *et al*., 2002). This was confirmed by XAD-7HP/XAD-4 resin fractionation which showed that the hydrophilic fraction was 47% of the total DOC content.

For the GAC column tests, coagulated water was collected from the same water treatment works and this had a NPOC content of 5.1 mg $L^{-1}$, $UV_{254}$ of 10 $m^{-1}$, pH 8 and alkalinity of 180 mg $L^{-1}$.

### 4.3.2 Fractionation

Amberlite XAD-7HP and Amberlite XAD-4 resins (Rohm and Haas, PA, USA) were used to fractionate 500 ml water samples and obtain three different fractions: hydrophobic, hydrophilic acid and hydrophilic non acid. Each type of resin (1.5 L) was slurried with NaOH (0.1 M; 1.5 L) for 24 hours. The resin was sequentially Soxhlet extracted for 48 hours each with methanol, acetonitrile and methanol again (1.8 L). The resin was packed into glass columns and rinsed with reverse osmosis (RO) water until the column effluent DOC was less than 2 mg/L. Each column (resin volume = 8 mL) was rinsed with NaOH (0.1 M), followed by ultrapure water and finally HCl (0.1 M). Water samples were filtered (0.45 µm, Fisher Scientific, UK) and pH 2 acidified using HCl. The samples were then passed through the XAD-7HP column where the hydrophilic fraction was collected at the effluent. The XAD-7HP effluent was then passed through the XAD-4 column where the hydrophilic non acid fraction was collected. DOC

of the initial water sample and the two effluents (hydrophilic and hydrophilic non acid) were measured and the abundance of hydrophobic fraction was determined by mass balance as the fraction did not elute from the XAD-7HP resin. All the chemical solutions and solvents were supplied by Fisher Scientific, UK.

### 4.3.3 Coagulation tests

Enhanced coagulation experiments were conducted using a jar tester (Phipps and Bird PB-900) [13]. 500 mL of water was introduced in each jar and the coagulant, ferric sulphate (Ferripol xl, EA West), was added at a dose of 5 mg $l^{-1}$ as Fe during the initial rapid mix (2 minutes at 200 rpm). HCl (1 M, Fisher Scientific, UK) was then added until pH was adjusted to 4.5 whilst stirring for an additional 1.5 minutes at 200 rpm. The jars were then stirred for 15 minutes at 30 rpm and left to settle for an additional 20 minutes before collecting the samples.

### 4.3.4 Photocatalytic oxidation

Photocatalytic oxidation experiments were undertaken in an annular stainless steel reactor of 5.2 cm internal diameter (WaterInnovate, UK) equipped with a medium pressure lamp of 4.7 cm external diameter (630 W, Hanovia, UK) (Figure 4.1). The distance between the inlet and the outlet was 27 cm while the UV lamp was 24 cm long. The reactor had a 1 mm wall-lamp gap which

corresponded to a treated volume of 0.1 L. Titanium dioxide (Aeroxide® $TiO_2$ P 25) with a specific surface area of 50 ± 15 $m^2.g^{-1}$, anatase : rutile ratio of 80/20 and an average primary particle size of 21 nm was purchased from Lawrence Industries (UK). A $TiO_2$ dose of 0.1 and 1 g $L^{-1}$ was added to a 15 L raw water (20 L container) equipped with a turbine to keep the $TiO_2$ particles in suspension. The resulting slurry was pumped vertically through the reactor. Air (20 L $min^{-1}$) was sparged inside the reactor through a diffuser situated at the bottom/inlet of the cylinder to enhance the reaction and provide mixing. A cooling jacket with circulating tap water maintained a stable temperature of 20°C in the system and prevented the UV lamp from overheating.

The optical thickness τ of the reactor defined as the product of the thickness of the annulus δ (1 mm), the mass absorption coefficient ε of $TiO_2$ (338 $m^2$ $kg^{-1}$) and the initial concentration c of $TiO_2$ (0.1 and 1 kg $m^{-3}$) was found to be equal to 0.03 and 0.3. These values are well below those reported by Li Puma and Brucato (2007) (in the range 1.8-4.4). The authors highlighted that an optical thickness of 3 resulted in a maximum efficiency. However the reaction kinetics and type of flow pattern should also be considered. For our reactor, this would imply a catalyst loading of 8.9 g $L^{-1}$.

The slurry was mixed in the dark for 15 min before a sample was collected. This corresponds to the dark adsorption data. The peristaltic pump was then adjusted in order to set the flow rate while the UV lamp was switched on. The flow rates were 200; 100; 20; and 10 mL $min^{-1}$ corresponding to a retention time of 0.5; 1; 5 and 10 minutes respectively. The retention time was defined as the

treatment time spent by the sample in the reactor (See inlet and outlet of the reactor, Figure 4.1). All samples were filtered through 0.2 µm filter (Fisher Scientific, UK) to remove the $TiO_2$ particles without altering the DOC content and stored at 4 °C prior analysis.

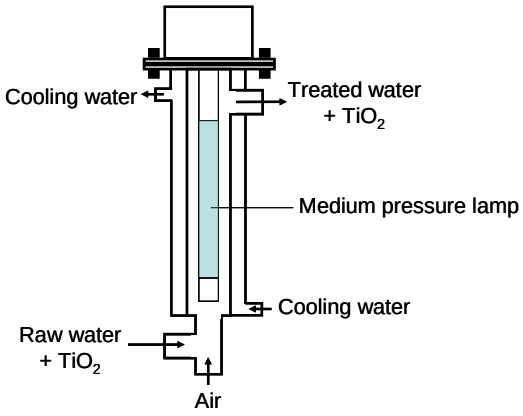



**Figure 4.1 Photocatalytic reactor.**

### 4.3.5 GAC batch isotherm test

GAC (Filtrasorb 400, Chemviron, UK) was crushed and sieved between 32 and 106 µm, washed thoroughly in deionised water and dried overnight at 110°C and kept in a dessicator until use. Carbon doses of between 0-2 g were added into 250 mL of water samples and stirred continuously on an orbital shaker (New Brunswick Scientific) at 200 rpm for 24 hours at 20°C. Water samples were filtered (0.2 µm, Fisher Scientific, UK) prior to analysis.

### 4.3.6 GAC column test

GAC was prepared as described in the isotherm tests except that the particle size was 150-200 µm. Prior to being loaded into the column (1 cm x 50 cm, Kinesis Ltd, UK), the GAC was boiled in ultrapure water for 10 minutes in order to replace the air in the carbon pores with water. The rapid small scale column test (RSSCT) (Standard Practice ASTM D6586-03) is widely used to predict the performance of full scale GAC adsorbers. This standard method allows a rapid determination of breakthrough curves by passing the water at a constant controlled rate down flow through a bed of a specially sized GAC and by sampling the column effluent regularly for NPOC, $UV_{254}$ and THMs analysis. The small amount of water required can be transported on the site of experiments. The results are specific to the water studied and biological degradation that may prolong the GAC bed life is not taken into account. The RSSCT design is based on the dispersed-flow pore surface diffusion model which maintains the similarity between small scale column (SC) and large scale column (LC) (Crittenden *et al*., 1987). Flowrate was set at 5 mL $min^{-1}$ allowing an Empty Bed Contact Time (EBCT) of 2.5 min. The mass of carbon was 4 g in all runs. Suspended solids in the feed is known to interfere with the operation of the column and to cause pressure drops so here water was prefiltered using a 0.4 µm chlorinated polyethylene (PE) membrane (Kubota, Japan). The set-up consisted of a metering pump (Watson Marlow Ltd, UK), a pressure indicator (Excel Pneumatics,UK), a glass column (1 cm x 50 cm, Kinesis Ltd, UK). 100 mL of column influent and effluent was collected at various time intervals and stored at 4°C prior to NPOC and THMFP analysis.

### 4.3.7 Biotreatment

The biodegradability of water samples was assessed using the method described by Joret and Levi (1986). Water samples of 250 mL were incubated during 5-8 days in duplicate with 50 g of post-ozone sand collected from Severn Trent Water, UK. The sand was stored in raw water with constant aeration and the bioactivity of the sand was verified using sodium acetate as a positive control. Biodegradable dissolved organic carbon (BDOC) is defined as the difference between the Initial NPOC and the minimum NPOC value after 5-8 days.

### 4.3.8 Analysis

A Shimadzu 5000A TOC analyser was used for determining NPOC content. Samples were acidified with 1% HCl (2 M) and the purge was 6 minutes. UV absorbance was measured at 254 nm wavelength using a Jenway 6505 UV/Vis spectrophotometer. The device was calibrated daily using deionised water. All samples were passed through a 0.2 µm filter paper (Fisher Scientific, UK) prior to $UV_{254}$ and DOC analyses. The removal and transformation of NOM could be determined by measuring change in High Performance Size Exclusion Chromatography or HPSEC (HPLC, Shimadzu VP Series, Shimadzu, Milton Keynes, UK). Larger molecules were eluted first and smaller molecules later. THM formation potential (THMFP) was measured following an adapted version of USEPA Method 551.1. Samples were buffered to pH 7 with phosphate buffer

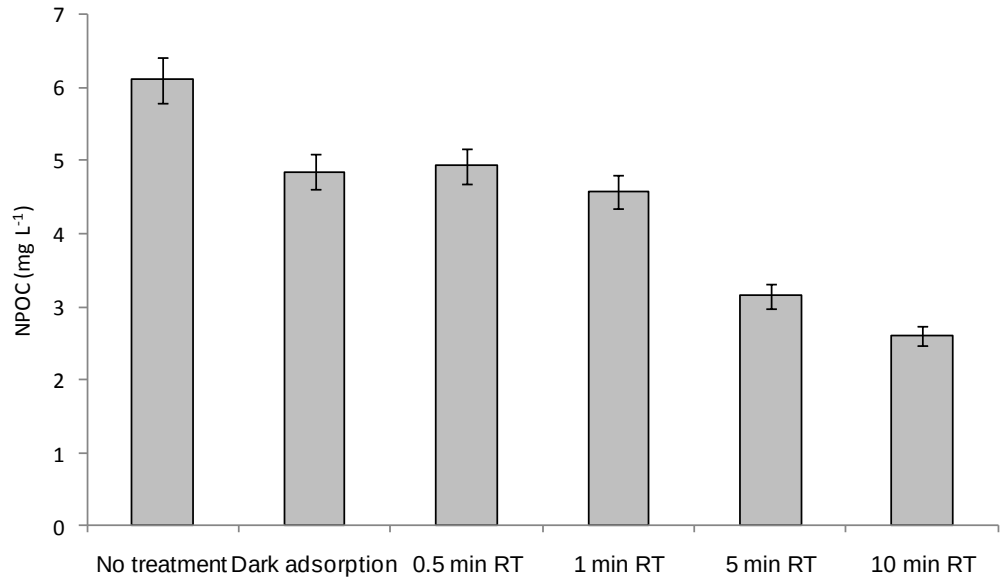
solution. Chlorine was added as sodium hypochlorite (Fisher Scientific, UK) at a dose of 5 mg $Cl_2$ per mg C. Chlorinated samples were incubated at 20 ºC for 24 hours in the dark in headspace-free 100 mL PTFE bottles. At the end of the reaction time, residual chlorine was quenched with sodium sulfite (Fisher Scientific, UK). THMs were extracted and derivatised with methyl tertiary-butyl ether (MTBE) at pH 4.5-5.5 and sodium chloride (both Fisher Scientific, UK). THMs were then measured using a gas chromatograph with micro electron capture detector (Agilent 6890 GC-ECD). Bromofluorobenzene at 30 µg $L^{-1}$ was used as internal standard. All chemicals were analytical grade or higher.

## 4.4 Results and discussion

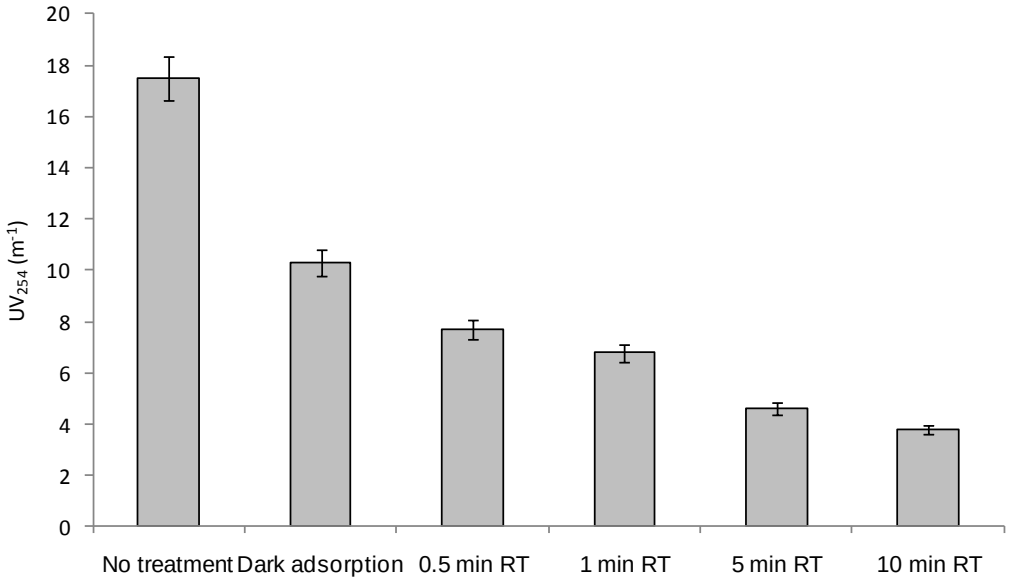
### 4.4.1 Photocatalytic oxidation

A series of initial experiments were undertaken to understand how treatable the organics were with photocatalytic oxidation and it was found that both removals of NPOC and $UV_{254}$ increased with increasing retention time and reached a maximum of 60% and 70% respectively after 10 minutes reaction time (Figures 4.2A and 4.2B). In comparison, enhanced coagulation achieved 50% NPOC removal and only 20% $UV_{254}$ removal. Greater removal of UV absorbing species by photocatalytic oxidation was observed and this indicates that those organics with conjugated or UV absorbing bonds were easier to degrade. We know that organic character can influence removal in photocatalytic oxidation, Eggins *et al.* (1997) for example showed that DOC from a humic acid solution at 100 mg

$L^{-1}$ was reduced at a rate three times slower than $UV_{254}$ absorbance. Liu *et al.* (2008) also reported high DOC and $UV_{254}$ removals (80% and 95% respectively) from a high colour (85 HU), high DOC level (10 mg $L^{-1}$) and low turbidity (2.3 NTU) raw surface water. Rosario-Ortiz *et al.* (2008) investigated the reactivity of ozone and hydroxyl radicals on isolated hydrophobic organic acids and non-isolated effluent organic matter respectively. They reported positive correlations between rate constants and bulk properties such as aromaticity, SUVA, fluorescence index and molecular weight (MW). Murray and Parsons (2004) found 81% and 96% as DOC and $UV_{254}$ removals respectively after treating a highly coloured raw water (7.5 mg $L^{-1}$ DOC; 38.1 $m^{-1}$ $UV_{254}$; 5.1 L $mg^{-1}$ $m^{-1}$ SUVA) using UV-C lamps (EEo of 0.27 to 0.83 kW h $m^{-3}$) and 5 g $L^{-1}$ of $TiO_2$. If we compare this final study with our own data then the higher removals are thought to be due to a combination of the aromatic nature of the organics present and the low alkalinity of the water as it is well known that bicarbonate and carbonate ions are scavengers of hydroxyl radicals.




(A)




(B)

**Figure 4.2 NPOC (A) and $UV_{254}$ (B) removal after UV/$TiO_2$ treatment (1g $L^{-1}$) at increasing retention times.**

Eggins *et al.* (1997) demonstrated that the degradation of hydrophobic organics occurred via a series of intermediates and not directly by mineralisation to

carbon dioxide and water molecules. Sarathy and Mohseni (2007) have previously highlighted changes in the molecular weight of the organic matter during UV/$H_2O_2$ treatment and they have shown the breakdown of large molecular weight organics into smaller compounds. Given the UV doses used here we do not expect complete mineralisation but we do see that larger MW species were preferentially removed (> 5 kDa and 3.5-5 kDa ranges) while smaller by-products (0.5-3.5 kDa) were formed and subsequently partially degraded (Figure 4.3).

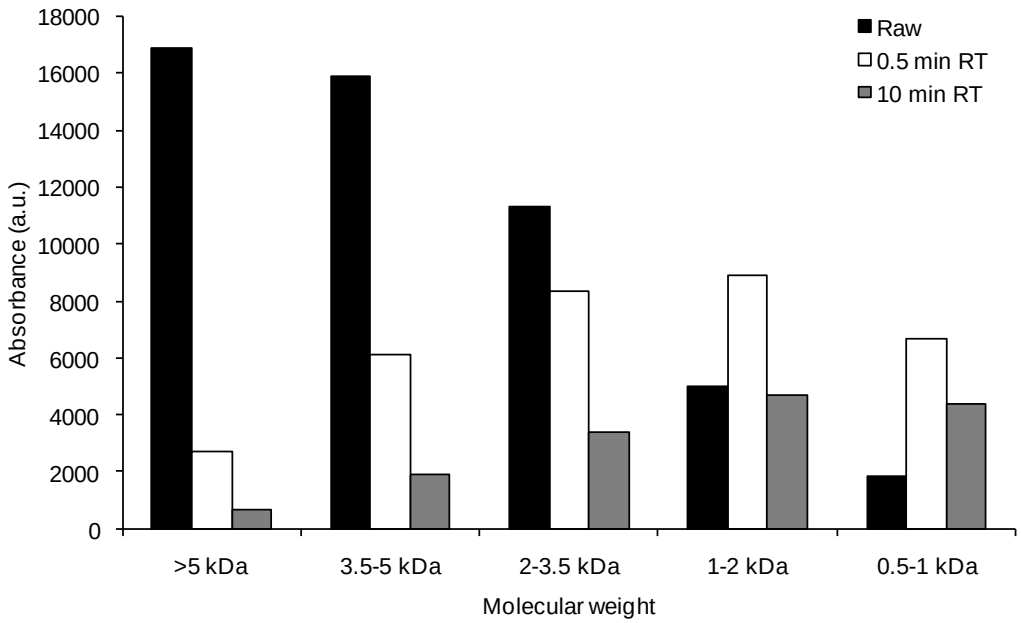



**Figure 4.3 Change in Average Molecular Weight (AMW) for raw water and water treated with photocatalytic oxidation at 0.5 min and 10 min RT (1g $L^{-1}$ as $TiO_2$).**

A key driver for this research was the reduction in the concentration of THMs formed during chlorination. Typically this is achieved by removing the precursor material and here the THMFP content (reported in µg $L^{-1}$) was reduced from 305 µg $L^{-1}$ in raw water to 144 µg $L^{-1}$ after 10 min treatment. This is consistent with previous research on synthetic humic acid solutions where 96% THMFP reduction was reported using a $TiO_2$ dose of 0.1 g $L^{-1}$ and an electrical energy per order (EEo) of 143 kW h $m^{-3}$ (Gerrity *et al*., 2009). However the THMFP content in µg mg $C^{-1}$ did not show any significant change with the treatment (Figure 4.4) which suggests that the oxidation by-products had the same chlorine reactivity as the NOM before treatment. Toor and Mohseni (2007) reported an increase of 74% in the dichlorohaloacetic acid formation potential (DCAAFP) in µg $L^{-1}$ of raw surface water after treatment with UV/$H_2O_2$ as did Bond *et al.* (2009a) who described the haloacetic acid formation potential (HAAFP in µg mg $C^{-1}$) increase of hydrophilic NOM surrogates specifically two amino acids, $_L$-glutamic acid and $_L$- leucine. They also showed how the molecular structure of organics significantly affected their reactivity with chlorine, where for example compounds such as resorcinol had the potential to form nearly 1 mole THM per mole whilst organics such as tannic acid formed less than 0.05 mole THM per mole (Bond *et al*., 2009b). Further research is required to investigate the nature of the by-products but it is clear that removal of these compounds should be considered after photocatalytic oxidation.

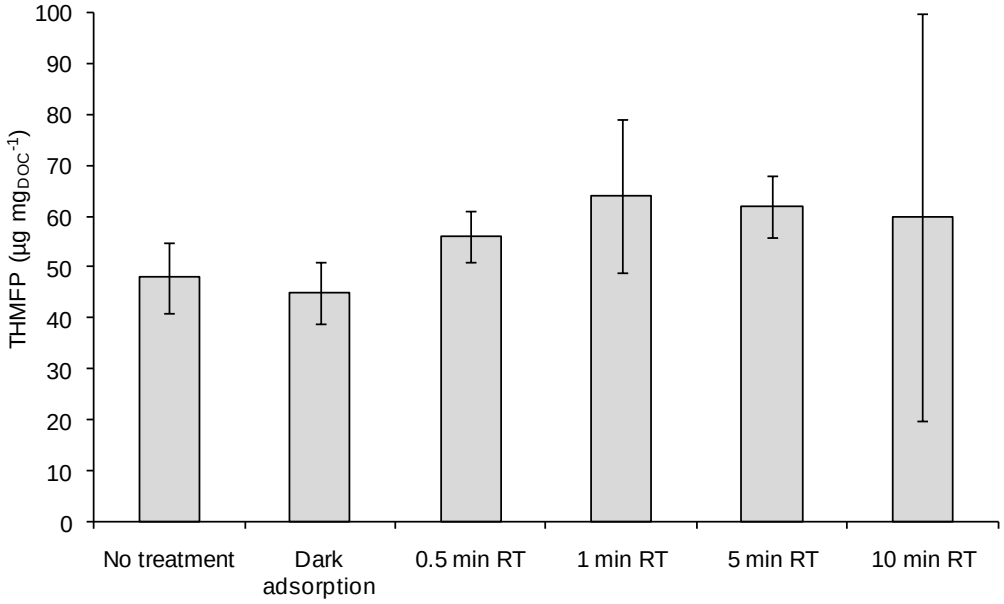



**Figure 4.4 THMFP (µg mgDOC$^{-1}$) after photocatalytic oxidation at increasing retention times (1g L$^{-1}$ as $TiO_2$, n=3).**

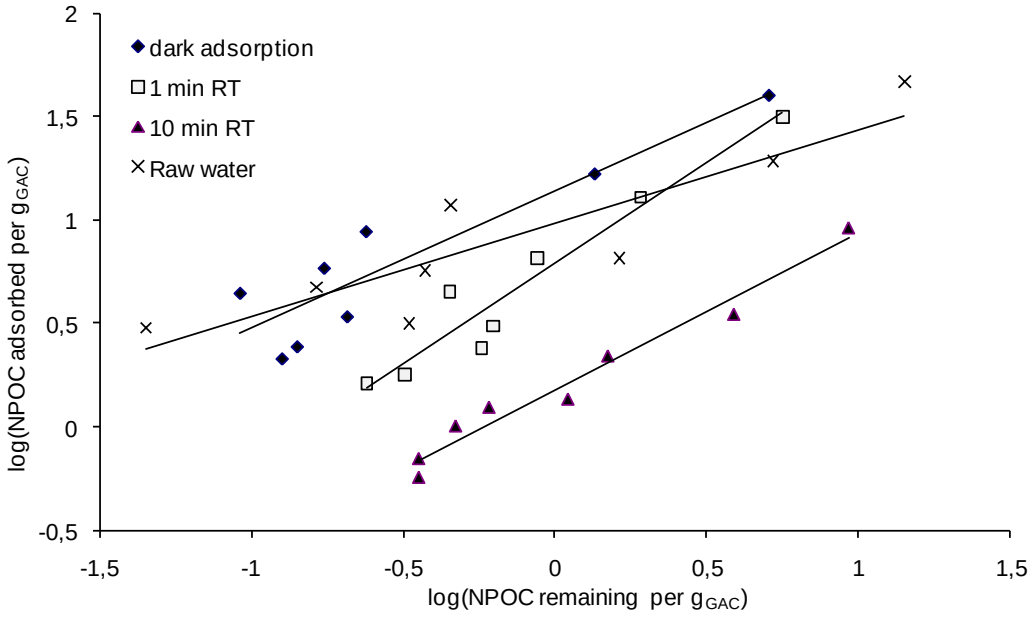
## 4.4.2 Photocatalytic oxidation followed by GAC

### *4.4.2.1 Batch tests*

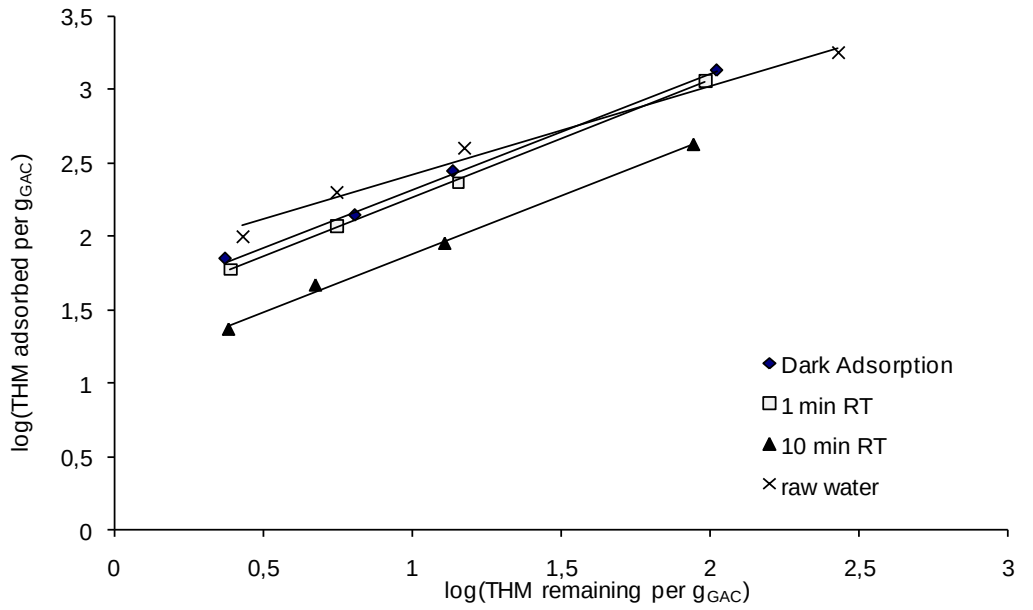
As photocatalytic oxidation is unlikely to achieve full mineralisation, a downstream process is needed to remove the oxidation by-products. Here we have combined photocatalytic oxidation with GAC treatment. Batch isotherm tests were conducted to follow the removal of both NPOC and THMFP (Figures 4.5A and 4.5B). The adsorption capacity parameter *Kf* for NPOC of the raw water was higher than those reported by Karanfil *et al*. (1999) where *Kf* for model compounds were 2.20-8.11 $mg_C$ per $g_{GAC}$. It was observed that adsorption capacity for THM precursors was significantly higher than adsorption capacity for NPOC whereas photocatalytic oxidation had a detrimental effect to

the adsorption capacity for both NPOC and THM precursors (Table 4.1). For instance, after 10 min RT, *Kf* decreased by 80% and 85% for THM precursors and NPOC respectively. It is known that surface chemistry plays a significant role in adsorption onto GAC and these results could be linked to an increase in hydrophilic character after photocatalytic oxidation. For example, the hydrophilic non acid fraction rose from 1.8 to 1.9 mg $L^{-1}$, the hydrophilic acid fraction decreased from 1.5 to 0.8 mg $L^{-1}$ and the hydrophobic fraction was reduced from to 3.7 to 1 mg $L^{-1}$. Bond (2009) reported lower adsorption of hydrophilic NOM model compounds on to GAC over hydrophobic ones such as resorcinol and Lambert and Graham (1995) observed that in batch tests, adsorption capacities of activated carbon were significantly reduced after ozonation of raw upland water (89-91% of fulvic acid) resulting from an increase in hydrophilicity and hence solubility of the organics.

(A)




(A)




(B)

**Figure 4.5. NPOC (A)and THMFP (B) adsorption isotherms after $TiO_2$ dark adsorption and UV/$TiO_2$ at different retention times (1 g $L^{-1}$ $TiO_2$).**

**Table 4.1. Modified Freundlich parameters.**

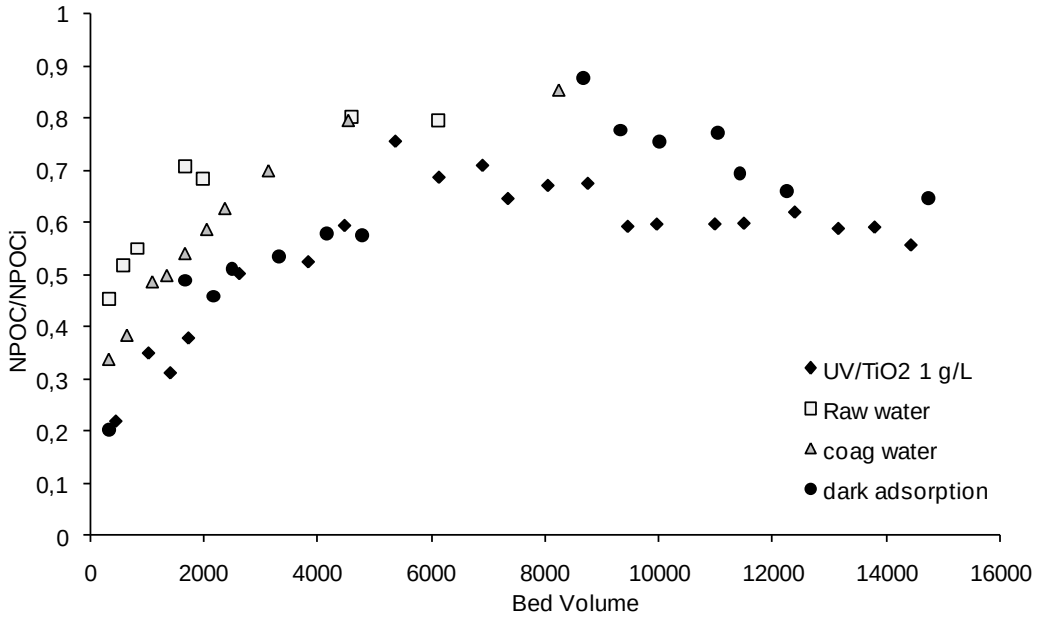
| | NPOC Isotherms | | | THMFP Isotherms | | |
|---|---|---|---|---|---|---|
| **Treatment** | **Kf** | **1/n** | **$R^2$** | **Kf** | **1/n** | **$R^2$** |
| Raw water | 9.54 | 0.45 | 0.80 | 64.56 | 0.60 | 0.98 |
| $TiO_2$ dark adsorption | 13.80 | 0.66 | 0.84 | 33.88 | 0.78 | 0.99 |
| UV/$TiO_2$; 1 min RT | 5.24 | 0.86 | 0.93 | 28.84 | 0.80 | 0.99 |
| UV/$TiO_2$; 10 min RT | 1.47 | 0.75 | 0.97 | 12.30 | 0.79 | 0.99 |

*4.4.2.2 Column tests*

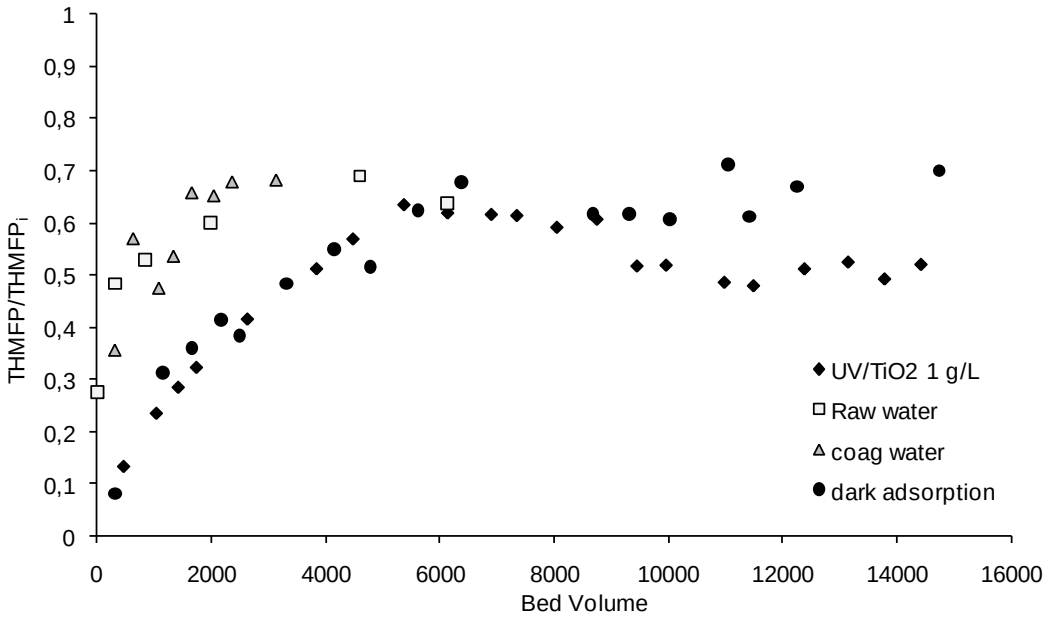
RSSCT were used here to predict the impact that different treatment combinations would have on the performances of GAC adsorbers. The tests were conducted for raw water, coagulated water, water after dark adsorption on $TiO_2$ and photocatalytic oxidation treated water at 1 g $L^{-1}$ and 1 min RT and it is clear that here photocatalytic oxidation improved both NPOC and THM precursor removal over coagulation alone (Figure 4.6 A and 4.6B). To illustrate, after 4000 BV, the removal of THMFP was 30% for the coagulated water versus 50% for the photocatalytic oxidation treated water. The total NPOC removed by GAC after 6000 BV was 45 mg for raw water which was equivalent to 363 kg at full scale while it was increased to 86 mg or 689 kg at full scale for photocatalytic oxidation treated water. The GAC bed life was also extended

after photocatalytic oxidation and 50% NPOC and THMFP breakthrough was reached after 15000 BV.

Chang *et al*. (2002) studied the removal of three NOM surrogates (humic acid, p-hydroxybenzoic acid and hydroquinone) with the combination of ozonation and GAC. In the case of humic acid, pretreatment at high ozone dose (6 mg $O_3$ per $g_{DOC}$) increased the adsorption capacity as humic molecules were broken down into smaller molecules and could diffuse more easily into the internal pore structures of the activated carbon. P-hydroxybenzoic acid and hydroquinone are small molecules and were not affected by size exclusion effect but their adsorption was controlled by surface chemistry. Ozonation resulted in an increase in the hydrophilicity and solubility of organics and therefore the affinity to GAC decreased. Our results though suggest that the size is controlling the adsorption on GAC in the dynamic columns tests while surface chemistry had a more significant impact in the batch tests. This is supported by the findings of Kaastrup and Halmo (1989) who reported that in the case of ozonation, organics adsorption on activated carbon was increased as long as the reduction in molecular size dominated the increase in polarity/hydrophilicity of preozonated humic molecules.




(A)




(B)

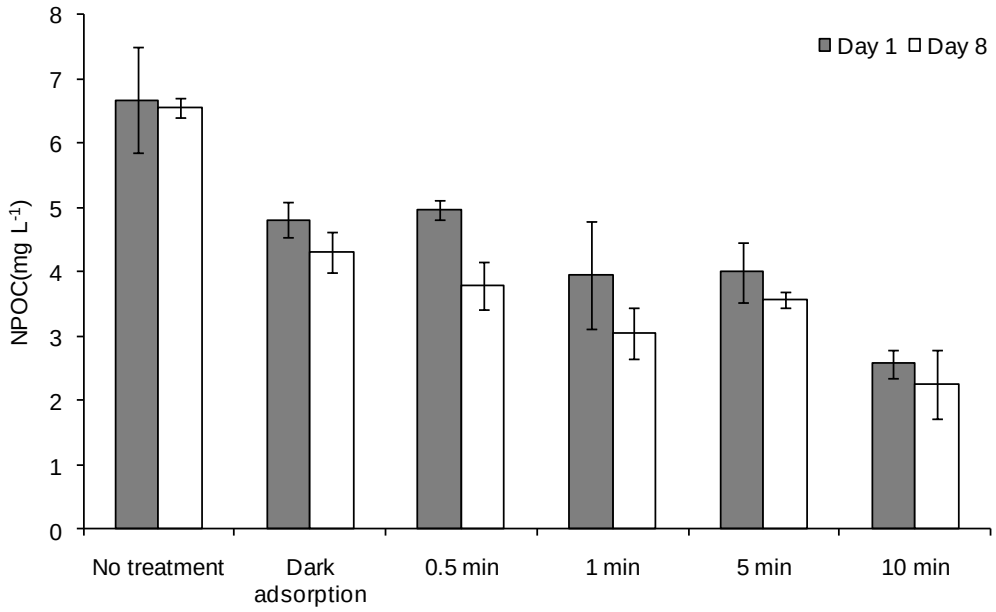
**Figure 4.6 Breakthrough curves in terms of NPOC (A) and THMFP (B) after various water treatments.**

### 4.4.3 Photocatalytic oxidation followed by biotreatment

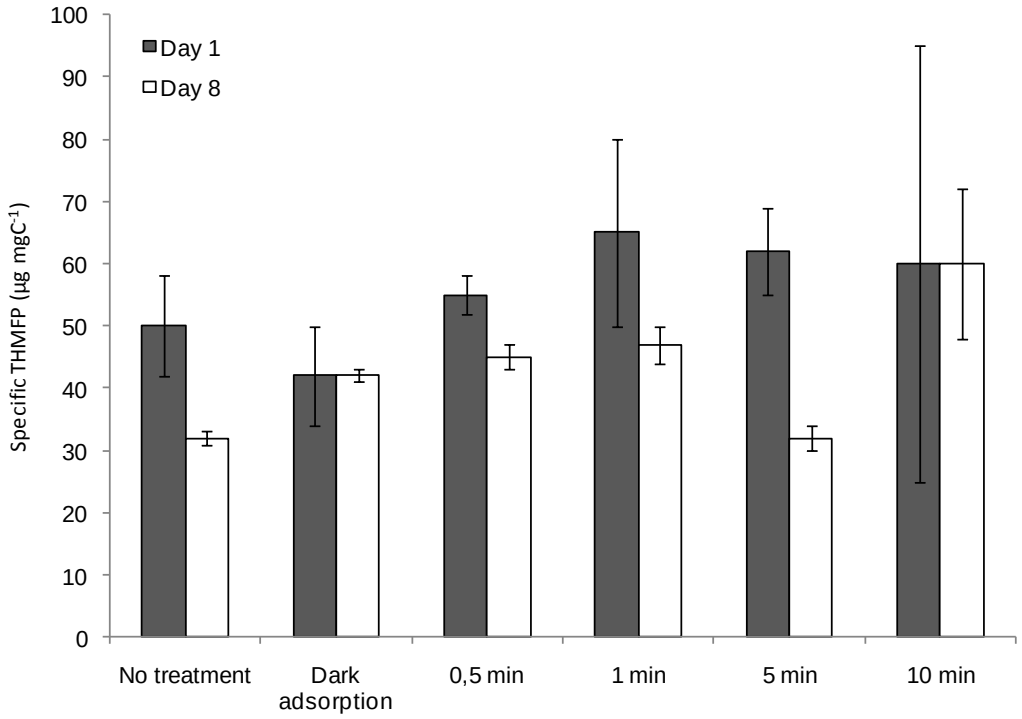
The combination of photocatalytic oxidation with biotreatment was also examined as treatment practice in the UK means that filtration or adsorption process is likely to be biologically active. Here biodegradability of both raw water and photocatalytic oxidation treated water by at different irradiation times (0-10 min) was assessed using a BDOC batch test. Results revealed that the raw water was not biodegradable and overall photocatalytic oxidation did not significantly enhance the biodegradability (Figure 4.7A). Thomson *et al*. (2002) investigated UV irradiation combined with biotreatment in the case of a high DOC water and also reported that only high UV doses (up to 26 J $cm^{-2}$) resulted in significant BDOC production, in this case 20% of the initial DOC.

THMFP of the UV irradiated samples was measured before and after contact with the bioactive sand to investigate the impact of the treatment on the THM precursor removal (Figure 4.7B). In raw water, although no mineralisation occurred, THM precursors were reduced by 28% after biotreatment. However, no further significant THMFP removal was observed when photocatalytic oxidation was used as a pretreatment except after 5 min RT where a removal of 60% was obtained compared with 28% removal by photocatalytic oxidation only. It is clear that the character of the organics plays a major role here as other authors have shown significant DBPFP removal when combining AOPs with biotreatment. For example, Miltner *et al*. (1992) reported 50% THMFP reduction after ozonation followed by biotreatment in batch tests while only 25% THMFP decrease was obtained after ozonation only (1 mg $O_3$ per $mg_{TOC}$); Toor

and Mohseni (2007) showed the synergetic effect of UV/$H_2O_2$ (0.5 J $cm^{-2}$) combined with biological activated carbon (BAC) columns as THMFP reduction reached 42% while THM precursors were only removed by 11% by BAC alone. Removals up to 50% using UV/$H_2O_2$ without BAC would require UV doses significantly higher than 1.3 J $cm^{-2}$.




(A)




(B)

**Figure 4.7 Impact of UV/$TiO_2$ on biotreatment in terms of NPOC (A) and specific THMFP (B)**

## 4.5 Conclusions

This study highlights the potential of treating reservoir waters rich in hydrophilic organic matter with photocatalytic oxidation. The removals of organics as measured with NPOC and $UV_{254}$ were significantly higher than those obtained by enhanced coagulation with metal salts. Photocatalytic oxidation has been shown to alter the structure of organics and the breakdown of high MW compounds into lower MW compounds was observed. Overall the concentration of THMs was reduced in the photocatalytic oxidation treated water although the oxidation by-products were found to be as reactive as the untreated organic

compounds. The benefits of combining photocatalytic oxidation with GAC have also been demonstrated here especially to remove the oxidation by-products. The combination of photocatalytic oxidation and biodegradation processes did not further enhance removal which indicates that the by-products formed were not easily degradable. The photocatalytic oxidation process did show significant performance benefits but at the detriment of energy costs and this should be a focus for future developments in this area.

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# 5 Photocatalytic oxidation of natural organic matter surrogates and the impact on trihalomethane formation potential.

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## 5.1 Abstract

Natural organic matter (NOM) consists of a complex mixture of organics and acts as precursors for a range of disinfection by-products (DBPs) including trihalomethanes (THMs). The characteristics of these precursors are still not well identified and here we have used a range of NOM surrogates that allows us to investigate how the characteristics of NOM relate to treatability with photocatalytical oxidation. Nine surrogates of NOM (5 amino acids, 2 carbohydrates, 2 phenolic compounds) were evaluated and the impact of retention time on dissolved organic carbon (DOC) and trihalomethane formation

potential (THMFP) was measured. Adsorption of the compounds onto $TiO_2$ was evaluated and electrostatic forces played a significant role in their removal although photocatalytic oxidation was found to be unselective. DOC and THMFP decreased significantly with retention time except for $_{L}$-leucine where the by-products formed during photocatalytic oxidation were significantly more reactive with chlorine than the parent compound.

## 5.2 Introduction

Disinfection by-products (DBPs) are a well known and unwanted result of reactions between organic matter, halide ions and disinfectants during potable water production. Since chlorine is the most commonly used disinfectant in water treatment, chlorinated DBPs and in particular trihalomethanes and haloacetic acids have received most research attention. Trihalomethanes (THMs) are often the major DBPs formed during chlorination but well over 500 other DBPs have been reported in the literature (Richardson *et al*., 1998). THMs were the first DBPs to be identified in drinking water (Rook, 1974), and have been regulated since 1979 in the USA to limit the risk they pose to human health. They are also the only group of chlorinated DBPs currently regulated in the UK where a maximum concentration value of 100 µg $L^{-1}$ at a consumers tap has been set for the sum of the concentrations of the four THMs (trichloromethane, dichlorobromomethane, dibromochloromethane and tribromomethane). Recent research has also looked at a wider range of DBPs formed in UK waters including haloacetic acids, haloacetonitriles and nitrosamines (Goslan *et al.,* 2009; Bougeard *et al.,* 2010).

Whilst water utilities have several available routes to minimise DBP formation, such as changing disinfection practice or position, it is the removal of the organic compounds or DBP precursors before disinfection that has received the greatest attention. Conventional treatment processes such as coagulation, ion exchange and MIEX have been shown to successfully remove the hydrophobic natural organic matter (NOM) (Fearing *et al*., 2004; Bolto *et al*., 2004, Mergen *et al*., 2008); however, the more hydrophilic compounds remain a challenge as these compounds have been shown to be significantly more difficult to treat (Sharp *et al*., 2006, Bond *et al.,* 2010). Advanced oxidation processes (AOPs) have been proposed as an alternative to conventional treatment processes and have been shown to break down a wide range of NOM compounds (Thomson *et al*., 2002, Goslan *et al*., 2006, Sarathy and Mohseni, 2007). AOPs are characterised by the generation of hydroxyl radicals (•OH) and whilst there are various ways of producing •OH, all these processes are thought to share the same method of degrading NOM, by means of electron transfer, hydrogen abstraction and OH addition to double bonds (Legrini *et al*., 1993). Given that the various reaction degradation pathways tend to be complicated and can also involve inorganic radicals, •OH are considered to react quickly and non-selectively with organic compounds and average second-order rate constants for reactions between NOM and •OH in seventeen waters has been reported as $3.9 \times 10^8$ $M^{-1}s^{-1}$ (Westerhoff *et al*., 1999). More recently rate constants were directly measured at $1\text{-}5 \times 10^8$ $M^{-1}s^{-1}$ for •OH and NOM reactions (Westerhoff *et al*., 2007) and are 3-4 orders of magnitude higher than for other oxidants used in water treatment (Bond *et al.,* 2010).

Photocatalytic oxidation has been considered as an alternative process for NOM removal as it has the potential to be a chemical free process where $TiO_2$ is recycled and no sludge is produced (Murray and Parsons, 2004; Gerrity *et al.,* 2009). Photocatalytic oxidation of natural waters have to date shown promising results where for example Liu *et al*. (2010) reported 80% DOC and 100% $UV_{254}$ removal from a surface water after 150 min treatment (20 W) at a dose of 0.1 g $L^{-1}$ of $TiO_2$ and importantly THMFP (in µg $L^{-1}$) was reduced by more than 90%. A pilot-scale study reported by Gerrity *et al.* (2009) showed how the treatment of two surface waters using a $TiO_2$ dose of 0.4 g $L^{-1}$ achieved a 90% reduction in THMFP although this was only achieved at high energy usage (320 kWh $m^{-3}$). Liu *et al*. (2008) followed the photocatalytic oxidation of NOM compounds in an Australian surface water using size exclusion chromatography (SEC-UV) and resin fractionation. They reported >75% removal of DOC and 100% removal of $UV_{254}$ after 120 minutes of treatment and showed that the NOM was degraded into smaller molecular weight compounds which were shown to be more hydrophilic in nature.

Espinoza and Frimmel (2009) recently investigated the selectivity of $UV/H_2O_2$ and photocatalytic oxidation in degrading natural organic matter. They used size exclusion chromatography (SEC-DOC) to follow changes in molecular size and found no evidence to support selective degradation of large molecular weight material during $UV/H_2O_2$ but did conclude that the degradation of NOM in photocatalytic oxidation does exhibit selectivity and that this is most likely due to the adsorption onto the $TiO_2$ surface. It is well known that the photocatalytic oxidation process is based on electron transfer that requires the adsorption of

the NOM compound onto the irradiated catalyst. Therefore it is important to study the role that the adsorption process can play in the whole photocatalytic oxidation process and we expect that adsorption will be controlled by both the size and chemical character of the organic compounds. Since the precise identity of compounds in natural waters is largely unknown, the use of surrogates is attractive as it enables the linking of explicit chemical and physical properties to treatability and also to DBPs formation. The aim of this study was to compare the impact that photocatalytic oxidation had on both organics removal and on THM formation. We have used a range of NOM surrogates to investigate if there was a link between removal and organic structure and these have been selected on the basis of the work of Croué *et al*. (2000) to include humic compounds, carboxylic acids, amino acids, proteins and carbohydrates.

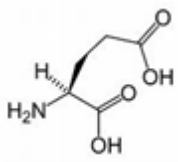
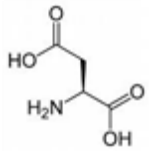
## 5.3 Materials and methods

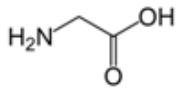
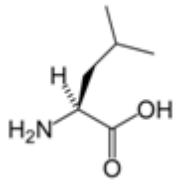
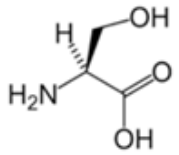
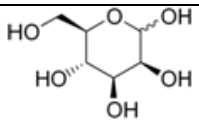
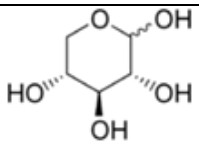
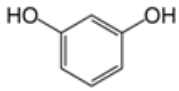
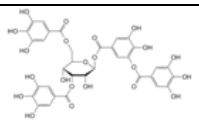
### 5.3.1 NOM surrogates

Model compounds ($_{L}$-glutamic acid, $_{L}$-aspartic acid, glycine, $_{L}$-leucine, $_{L}$-serine, $_{D}$-mannose, $_{D}$-xylose, tannic acid and resorcinol) were obtained from Sigma Aldrich (UK) and were all analytical purity or higher. The model compounds can be classified as hydrophobic or hydrophilic based on their log $K_{ow}$ values being above or below zero respectively, and as anionic or neutral at pH 7 based on their pKa value (Table 5.1). Deionised (DI) water with an electronic resistance of 15 MΩ (PureLab Classic™, Elga) was used to prepare the stock and test

solutions. The initial DOC concentration of all model compound solutions was 6 mg $L^{-1}$ except for tannic acid (initial DOC 4.5 mg $L^{-1}$). Bond *et al.* (2009b) has also recently described the fractionation behaviour of these nine compounds according to a procedure commonly used in NOM characterisation where the material is split into four fractions: hydrophobic acid (HPOA), transphilic acid (TPHA), hydrophilic (HPI) and hydrophobic neutral (HPON). Tannic acid and resorcinol were defined as HPOA whilst the seven other compounds behaved as HPI. Humic acids typically comprise around 50% of the NOM in surface water and this can include resorcinol structures (Norwood *et al*., 1987). Amino acids are typically present at mean levels of 0.3 mg L-1 in surface waters, representing some 2-5% of the total DOC of which glutamic acid, glycine, serine and aspartic acid are considered the most abundant species (Thurman, 1985). Carbohydrates are typically present in surface waters at mean concentrations of 0.5 mg.L-1 (Thurman, 1985) although a recent study found concentrations of 1 mg $L^{-1}$ , or 50% of the DOC in a Spanish river (Navalon *et al.,* 2008).

**Table 5.1 Model compounds properties**

| Compound | Structure | Log $K_{ow}$ | MW g $mol^{-1}$ | $pK_1$, $pK_2$, $pK_3$ | NOM Classification | Chemical group | $E_{(254\ nm)}$ $cm^{-1}$ L mg $C^{-1}$ |
|---|---|---|---|---|---|---|---|
| $_L$-Glutamic acid |  | -3.69 | 147 | 2.16, 4.15, 9.58 | Hydrophilic anionic | Amino acid | 0.000 |
| $_L$ -Aspartic acid |  | -3.89 | 133 | 1.95, 3.71, 9.66 | Hydrophilic anionic | Amino acid | 0.000 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Glycine |  | -3.21 | 75 | 2.34, 9.58, NA | Hydrophilic neutral | Amino acid | 0.000 |
| $_{L}$-Leucine |  | -1.52 | 131 | 2.32, 9.58, NA | Hydrophilic neutral | Amino acid | 0.000 |
| $_{L}$-Serine |  | -3.07 | 105 | 2.13, 9.05, NA | Hydrophilic neutral | Amino acid | 0.000 |
| $_{D}$-Mannose |  | -3.24 | 180 | 12.0, NA, NA | Hydrophilic neutral | Carbo-hydrate | 0.000 |
| $_{D}$-Xylose |  | -1.98 | 150 | 12.1 NA, NA | Hydrophilic neutral | Carbo-hydrate | 0.000 |
| Resorcinol |  | 0.8 | 110 | 9.32, NA, 11.1 | Hydro-phobic neutral | Phenolic | 0.045 |
| Tannic Acid |  | 13.3 | 1701 | 3.2, NA, 8.7 | Hydro-phobic anionic | Phenolic | 0.006 |

*E: mass extinction coefficient*

### 5.3.2 Photocatalytic oxidation

Photocatalytic oxidation experiments were undertaken in an annular reactor (WaterInnovate, UK) equipped with a medium pressure lamp (630 W, Hanovia, UK) (Figure 5.1). A titanium dioxide (Aeroxide® $TiO_2$ P 25) dose of 1 g $L^{-1}$ was added to a 15 L model compound solution at pH 5.5 in a container (20 L) equipped with a turbine to keep the $TiO_2$ particles in suspension. The resulting slurry was pumped vertically through the reactor. Air (20 L $min^{-1}$) was sparged inside the reactor through a diffuser situated at the bottom/inlet of the cylinder to enhance the reaction and provide mixing. A cooling jacket with circulating tap water maintained a stable temperature of the system at 20°C and prevented the UV lamp from overheating. Prior to the UV light being switched on, the model compound/$TiO_2$ slurry was stirred for 15 min in the dark and a first sample was collected which we have described here as the dark adsorption data. The UV light was then switched on and the peristaltic pump was successively adjusted in order to obtain a flow rate of 200; 100; 20; 10 mL $min^{-1}$ by measuring the water volume at the outlet within 1 min. The working volume in the reactor being 100 mL, the flow rates of 200; 100; 20; 10 mL $min^{-1}$ correspond to a retention time of 0.5; 1; 5 and 10 minutes respectively. After adjustment of each flow rate, a 100 mL sample was collected, filtered through 0.2 µm filter (Fisher Scientific, UK) to remove the $TiO_2$ particles and stored at 4 °C prior analysis.

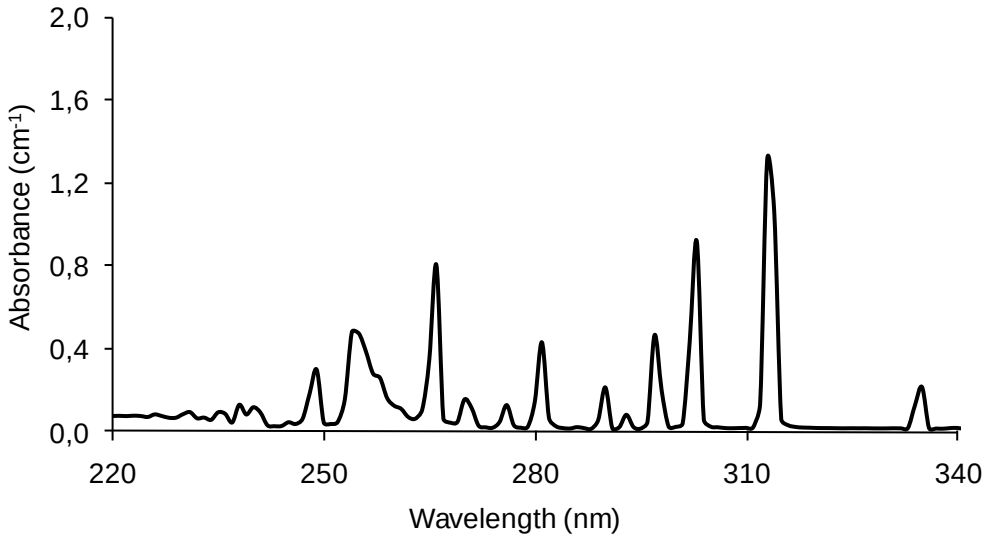



**Figure 5.1 Emission spectrum medium pressure UV lamp**

### 5.3.3 Analysis

A Shimadzu 5000A TOC analyser was used to determine the DOC. Values reported here represent the average of two samples, each measured three times. Error bars represent the standard deviation between the average measurements for two samples. Here we report the value of the chloroform formation potential ($CHCl_3FP$) as only chloroform contributed to the total THMFP since originals samples had a low level of bromide; specific $CHCl_3FP$ in µg $mg_{DOC}^{-1}$ is defined as the ratio of $CHCl_3FP$ in µg $L^{-1}$ by the corresponding DOC in mg $L^{-1}$. $CHCl_3FP$ was measured following an adapted version of USEPA Method 551.1. Samples were buffered to pH 7 with phosphate buffer solution. Chlorine was added as sodium hypochlorite (Fisher Scientific, UK) at a dose of 5 mg $Cl_2$ per $mg_{DOC}$. Chlorinated samples were incubated at 20 ºC for 24 hours in the dark in headspace-free 100 mL PTFE bottles. At the end of the

reaction time, residual chlorine was quenched with sodium sulfite (Fisher Scientific, UK). $CHCl_3$ were extracted and derivatised with methyl tertiary-butyl ether (MTBE) at pH 4.5-5.5 and sodium chloride (both Fisher Scientific, UK). Bromofluorobenzene at 30 µg $L^{-1}$ was used as internal standard. All chemicals were analytical grade or higher. $CHCl_3$ were then measured using a gas chromatograph with micro electron capture detector (Agilent 6890 GC-ECD). Limit of detection (LOD) for the trichloromethanes $CHCl_3$ was 0.028 µg $L^{-1}$ and the minimum reporting level (MRL) was 0.084 µg $L^{-1}$. Values reported here represent the average of two samples, each analysed twice. Error bars represent the standard deviation among the measured THMs concentrations of the two samples.

## 5.4 Results and Discussion

### 5.4.1 DOC removal

#### *5.4.1.1 Dark adsorption*

We have investigated the removal of each model compound during the initial dark adsorption period to identify relationship between chemical character and adsorption. The hydrophobic anionic tannic acid was the only compound significantly removed during dark adsorption, with 85% removal after 15 minutes (Figure 5.1C).

The two hydrophilic anionic species, $_L$-glutamic and $_L$-aspartic acid showed moderate removal of 25% and 40% respectively (Figure 5.1A). The other compounds did not show any significant change in the DOC content during this adsorption stage. Three mechanisms have been used to explain the adsorption of organic compounds onto $TiO_2$ surface: electrostatic adsorption, specific adsorption by covalent bond in the case of formation of a complex and hydrophobic effects (Lambert, 2008). We therefore expect that a relationship would exist between removal and compound charge and here tannic acid which has multiple negative charges is better removed when compared to the two hydrophilic anionic surrogates, each having a single negative charge and all other compounds which are neutral under ambient pH conditions. Eggins *et al.* (1997) and Palmer *et al.* (2002) both reported significant removal of the large hydrophobic compound humic acid after dark adsorption onto $TiO_2$ and highlighted the importance of high molecular weight of humic acid and the large number of functional groups binding on $TiO_2$. Tannic acid also exhibits a surface charge of -1 $mol_C$ $mol^{-1}$ at the studied pH (5.5) which suggests that adsorption on $TiO_2$ occurred via attractive electrostatic interactions unlike for example resorcinol which is uncharged at pH 5.5 (An and Dultz, 2007).

Paszti and Guczi (2009) did show that anionic amino acids, such as $_L$-aspartic acid and $_L$-glutamic acid, exhibit a significant affinity towards hydrophilic $TiO_2$ and that both the carboxylic groups of the $_L$-aspartic acid molecule were coordinated to the $TiO_2$ surface forming an ordered adsorbate layer. Bond *et al.* (2010) reported the adsorption of the same group of model compounds onto granular activated carbon (GAC) and also showed that tannic acid and amino

acids such as aspartic acid exhibited higher adsorbability than the other compounds. However, resorcinol showed different behaviour and had a high adsorption capacity for GAC whilst here we have seen no significant affinity with $TiO_2$. This suggests that although polarity, hydrophobicity and size are the limiting parameters in GAC adsorption, these electrostatic interactions are likely to be the limiting parameters for $TiO_2$ adsorption. Rincon *et al.* (2001) proposed that the absence of interaction between $TiO_2$ and resorcinol was due to the absence of –OH group in ortho position on the benzene ring. Unlike resorcinol, the aromatics rings of tannic acid can interact with the hydrophobic sites on $TiO_2$ surface since the –OH groups are in ortho position. Lam et al. (2007) later used Fourier transform infrared (FTIR) analysis to show how $TiO_2$ which had been in contact with resorcinol was identical to virgin $TiO_2$ indicating the absence of surface interaction.

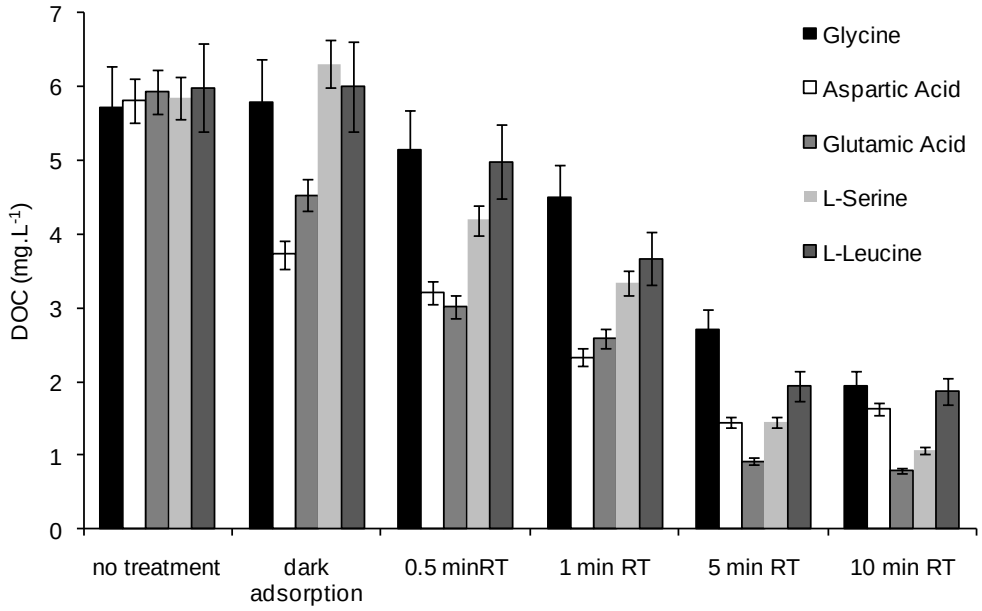
### 5.4.2 Photocatalytic oxidation

Following the significant DOC reduction observed during the dark adsorption phase, tannic acid remained at around 0.5 mg $L^{-1}$ after photocatalytic oxidation (Figure 5.1C). In comparison the concentration of the other hydrophobic compound, resorcinol, was reduced up to 90% after 1 minute photocatalytic oxidation and reached a plateau at 0.5 mg $L^{-1}$ after 5-10 minutes. The results compare well with Duczmal and Sobczynski (1999) study that reported 80-85% DOC removal after 3 hour irradiation (medium pressure UV lamp of 180 W) and a $TiO_2$ dose of 0.3 g $L^{-1}$. The DOC of all the other compounds was reduced

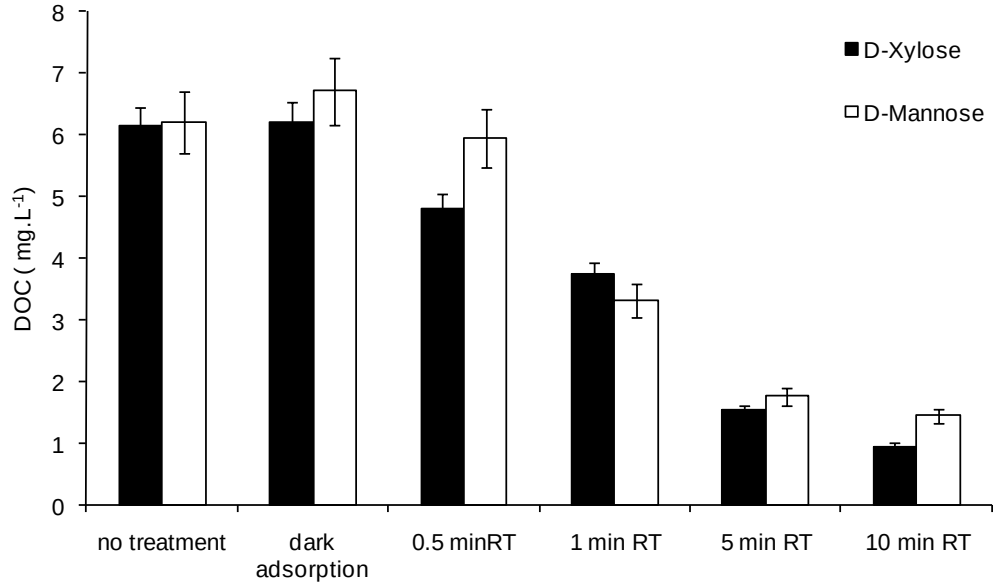
significantly during the first minute of treatment and reached a plateau at 1-2 mg $L^{-1}$ from 5 to 10 minutes indicating that complete mineralisation was not achieved. This is consistent with Horikoshi *et al*. (1998) who reported 98% DOC degradation for $_L$-serine after 300 min irradiation time (75 W) and 2 g $L^{-1}$ of $TiO_2$ and Szabo-Bardos *et al*. (2006) who observed 80% $_L$-aspartic acid removal after 200 min irradiation time (40 W) and 1 g $L^{-1}$ of $TiO_2$.

Among the hydrophilic compounds, $_L$-glutamic acid, $_L$-aspartic acid, $_L$-serine and $_D$-mannose exhibited the highest removal after 1 minute with between 42% and 59% corresponding to 2.5-3.5 mg $L^{-1}$ (Figures 5.1A and 5.1B). DOC decrease from the initial values. Glycine, $_L$-leucine and $_D$-xylose showed lower DOC reduction after photocatalytic oxidation treatment ranging from 21% to 39% after 1 minute photocatalytic oxidation. Bond *et al*. (2009a) also reported that glycine had the lowest reactivity of these nine compounds when treating with UV-C, VUV and UV/$H_2O_2$. The degradation of amino acids by AOPs has previously been studied in some detail by Le Lacheur and Glaze (1996) who proposed that this was because glycine forms a less stable secondary radical while the other amino acids form more stable tertiary radicals. Tran et al. (2006) demonstrated that amino acids containing –OH in their side chain like $_L$-serine, $_L$-glutamic acid and $_L$-aspartic acid were more amenable to photocatalytic oxidation. When comparing photocatalytic oxidation with UV/$H_2O_2$ oxidation reported by Bond *et al*. (2009a), only glycine stands out as being significantly different. Photocatalytic oxidation achieved a 66% reduction in DOC after 10 minutes whereas oxidation via UV/$H_2O_2$ achieved a 23% reduction at a dose of 23 J $cm^{-2}$.

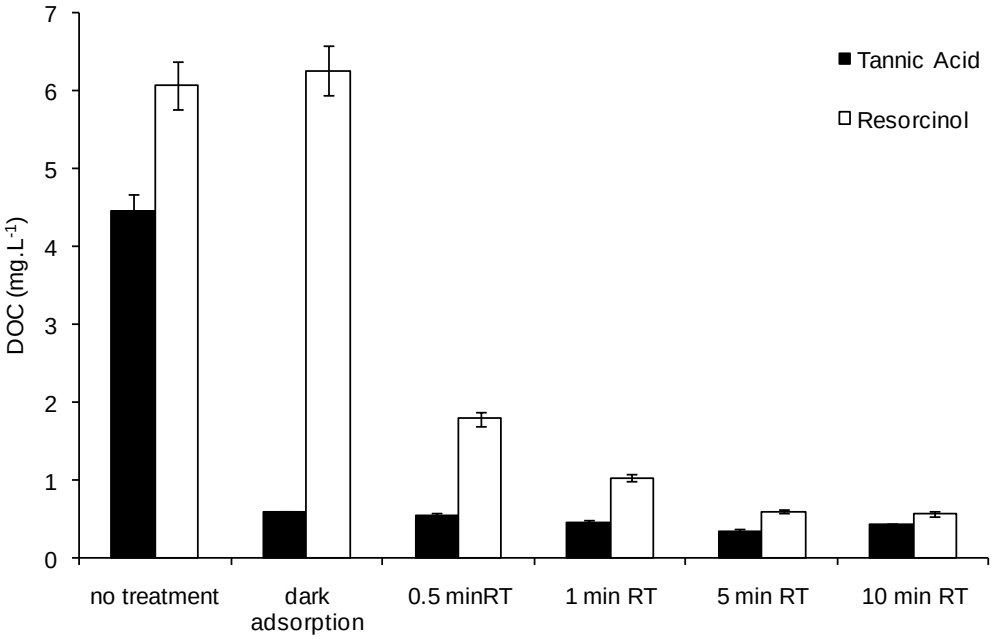
Espinoza and Frimmel (2009) identified a link between NOM molecular weight and removal during photocatalytic oxidation. Here it is clear that adsorption of the model compounds on to $TiO_2$ was selective but when considering the oxidation process then there was no evidence to support selectivity. Aside from $_D$-mannose, $_L$-leucine and $_L$-aspartic acid, all the compounds were reduced to below 1 $mg_{DOC}$ $L^{-1}$, well below coagulation alone (Bond *et al*., 2010).




(A)




(B)




(C)

**Figure 5.2 Impact of retention time on DOC removal during photocatalytic oxidation of amino acids (A), carbohydrates (B) and hydrophobic compounds (C).**

### 5.4.3 Chloroform formation potential ($CHCl_3FP$)

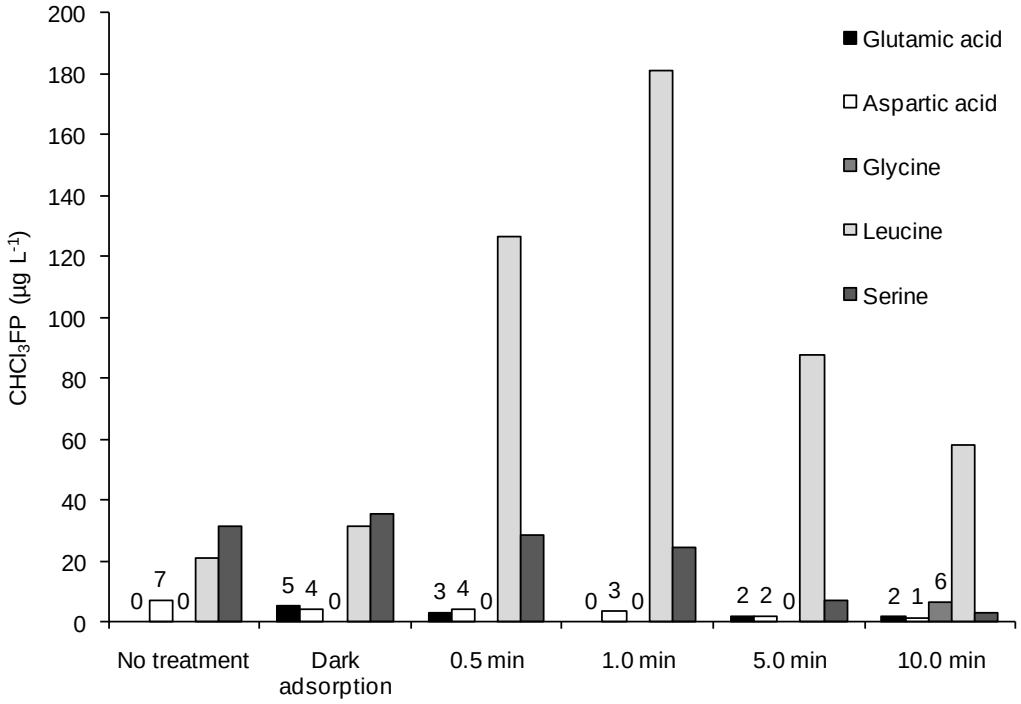
Chlorine reacts with aromatic compounds by electrophilic substitution and we know that in the presence of an electron-donating and ortho-para directing group (for example phenol) stepwise chlorination occurs at the 2, 4, and 6 positions respectively, to give THM formation. Major reactive sites in humic compounds such as tannic acid are thought to be where a carbon is between two hydroxyl groups such as seen in the resorcinol compound; these are being widely reported as the most important THM precursors (Bond *et al*., 2009b). Here the chlorination of the model compounds produced very different levels of $CHCl_3FP$ with resorcinol and tannic acid forming for example 8776 and 129 µg $L^{-1}$ respectively (Figures 5.2C and 5.2D). The $CHCl_3FP$ of all the other compounds were below 40 µg $L^{-1}$ which is consistent with recent reports for both amino acids (Hong *et al*., 2009) and carbohydrates (Navalon *et al*., 2008) (Figures 5.2A and 5.2B). Only tannic acid showed significant change during the dark adsorption stage where the $CHCl_3FP$ fell (in line with DOC removal) from 129 µg $L^{-1}$ to 15 µg $L^{-1}$ after 15 minutes. After photocatalytic oxidation, the specific $CHCl_3FP$ of tannic acid remained at 25 µg $mg_{DOC}^{-1}$ which could suggest that either no additional reaction occurred of that the by-products formed had a similar reactivity towards chlorine as tannic acid itself (Figure 5.3D).

Photocatalytic oxidation of resorcinol did though show significant impact on the specific $CHCl_3FP$ which decreased from 1400 to 150 µg $mg_{DOC}^{-1}$ indicating that formation of photocatalytic oxidation by-products of lower reactivity. In the case of resorcinol complete mineralisation was not achieved but it is clear that the

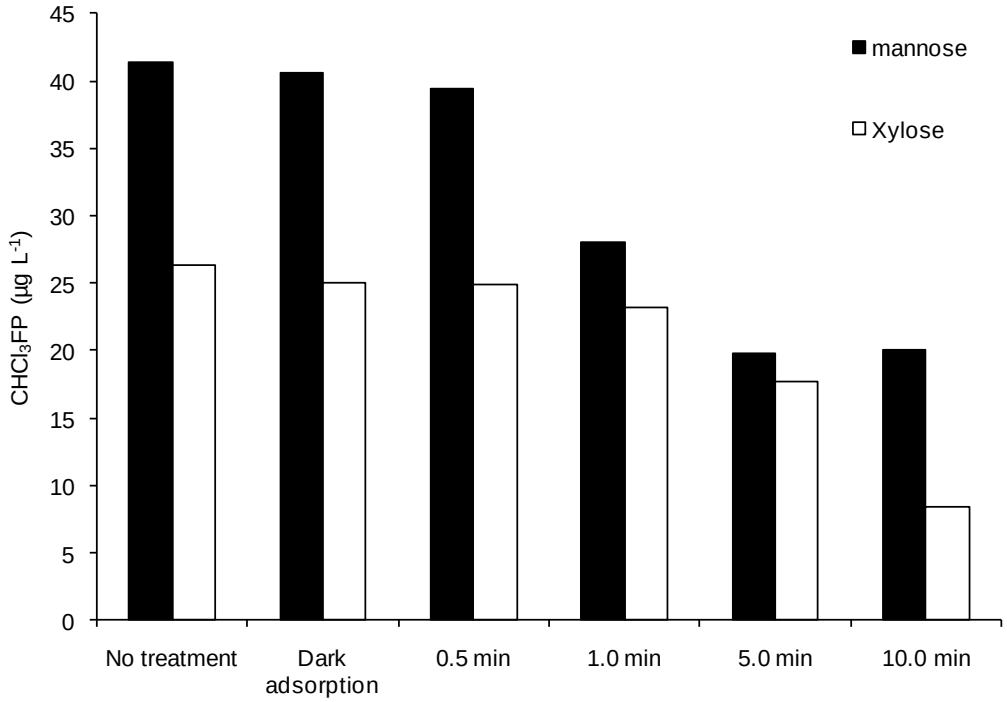
photocatalytic oxidation changed the chemical structure of the compound (Figure 5.3A-C). Whilst a number of specific by-products of NOM oxidation with ozone and UV (Corin *et al.,* 1996) have been reported, little is known about by-products formed during photocatalytic oxidation. Liu *et al*. (2008) reported that aldehydes and ketones were typical intermediates formed during photocatalytic oxidation of large aromatic substances and as the process proceeded these compounds would be oxidised to form carboxylic acids. For example, a number of authors have identified resorcinol oxidation by-products including 1,2,3-trihydroxybenzene and 1,2,4-trihydroxybenzene (Duczmal *et al.,* 1999; Lam *et al.,* 2007; Arana *et al.,* 2008). These compounds are known to be significantly less reactive with chlorine (THMFP of 2 µg $mg_{DOC}^{-1}$ and 257 µg $mg_{DOC}^{-1}$ respectively) when compared to the highly reactive resorcinol so the reduction in overall formation potential is expected.

Liu *et al.* (2008) reported the formation of short chain aldehydes and ketones during the photocatalytic oxidation of surface water NOM fractions and identified increases in the concentration of formaldehyde and acetone. Acetone is a significant THM precursor (564 µg $mg_{DOC}^{-1}$) while oxalic acid known as the major product of NOM oxidation by UV and ozone has a THMFP of 2 µg $mg_{DOC}^{-1}$. More simple monobasic acids cited as oxidation by-products of NOM do not contain functionalities thought to be reactive DBP precursors (Singer, 1999). No change in chlorine reactivity was observed after photocatalytic oxidation of $_{D}$-mannose, $_{D}$-xylose, $_{L}$-glutamic acid, $_{L}$-aspartic acid, $_{L}$-serine and glycine, all of whom had reactivity of less than 5 µg $mg_{DOC}^{-1}$. $_{L}$-leucine did exhibit significantly different behaviour and here the $CHCl_3FP$ increased from an initial value of 2 µg

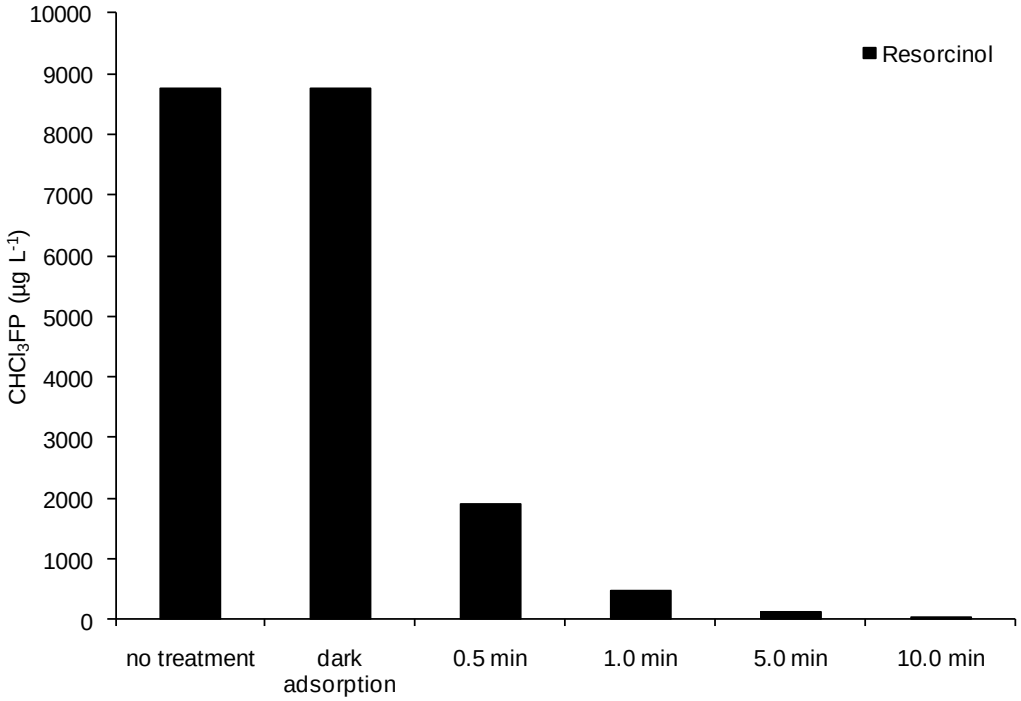
$mg_{DOC}^{-1}$ up to a maximum of 50 µg $mg_{DOC}^{-1}$ after 1 minute of photocatalytic oxidation. After 10 minutes of photocatalytic oxidation the reactivity decreased down to 30 µg $mg_{DOC}^{-1}$. This shift to enhanced THM levels post-oxidation processes has literature precedent as both Liu *et al.* (2010) and Gerrity *et al.* (2009) have reported an increase in THMFP during photocatalytic oxidation of hydrophilic rich surfaces water. These hydrophilic rich waters are likely to contain elevated concentrations of amino acids as a result of algal or wastewater influence. Bond *et al*. (2009a) also reported an increase in HAAFP of both $_L$-glutamic acid and $_L$-leucine after VUV and UV/$H_2O_2$ treatment. For $_L$-glutamic acid the increase in HAAFP was primarily associated with dichloroacetic acid (DCAA) rather than trichloroacetic acid (TCAA) which are thought to have similar precursors to THMs. No data was presented for $_L$-leucine but structurally cleavage of the $(CH_3)_2CH$- group may act as a precursor for $CHCl_3$ formation.


200
180
160
140
120
100
80
60
40
20
0
CHCl3FP (µg L-1)
Glutamic acid
Aspartic acid
Glycine
Leucine
Serine
0 7 0
5 4 0
3 4 0
0 3 0
2 2 0
2 1 6
No treatment
Dark adsorption
0.5 min
1.0 min
5.0 min
10.0 min

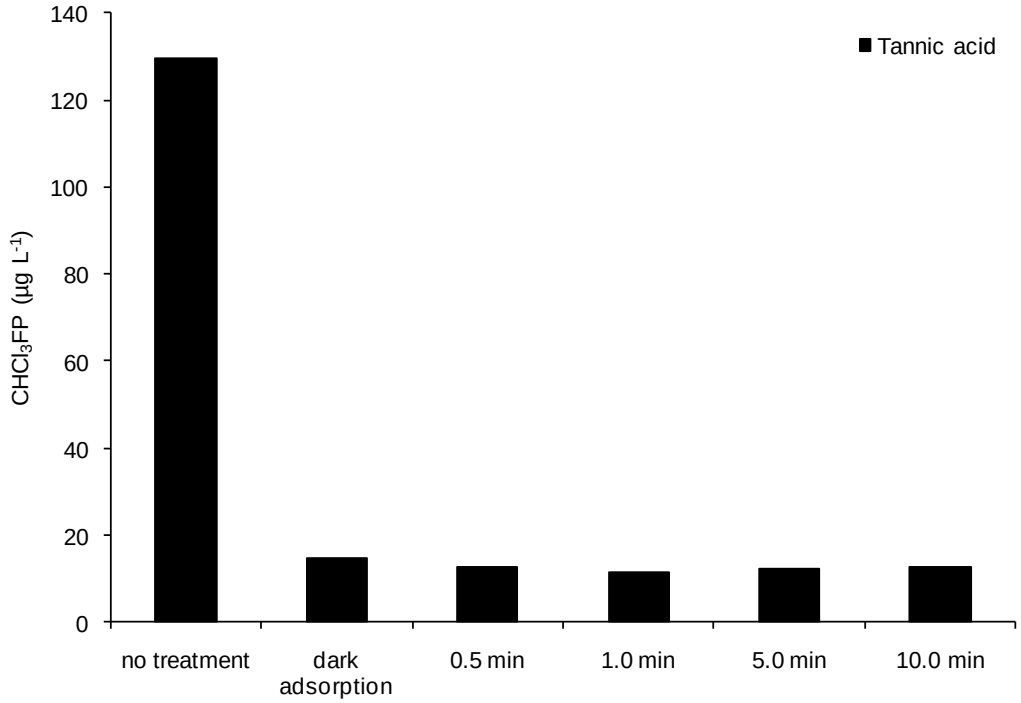
5.2 (A)


45
40
35
30
25
20
15
10
5
0
CHCl3FP (µg L-1)
mannose
Xylose
No treatment
Dark adsorption
0.5 min
1.0 min
5.0 min
10.0 min

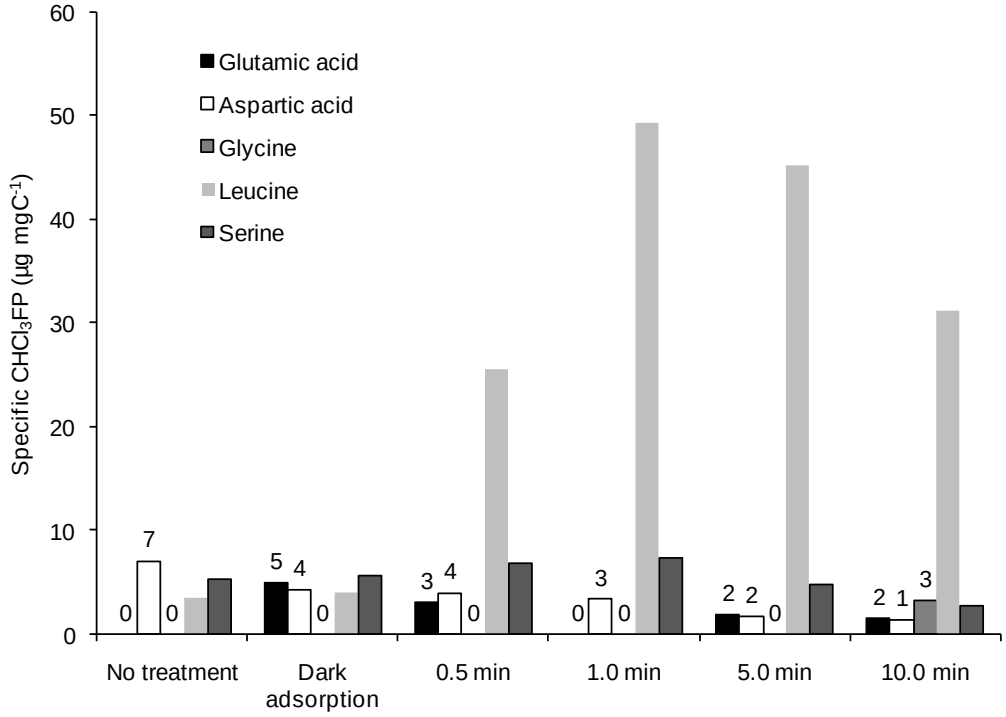
5.2 (B)


10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
CHCl3FP (µg L-1)
Resorcinol
no treatment
dark adsorption
0.5 min
1.0 min
5.0 min
10.0 min

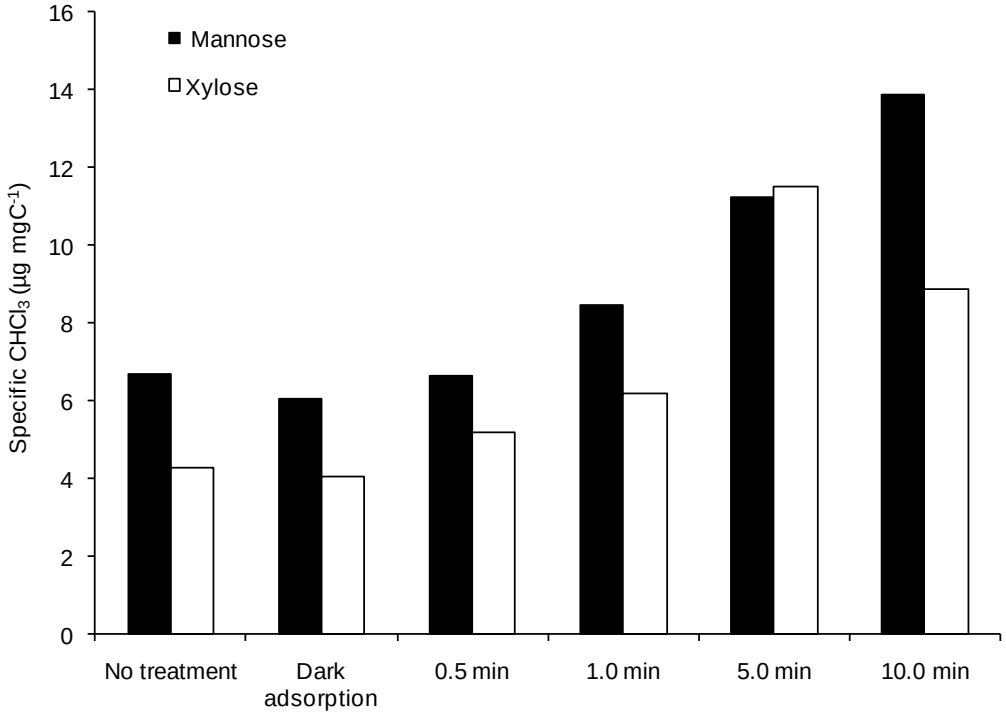
5.2 (C)


140
120
100
80
60
40
20
0
CHCl3FP (µg L-1)
Tannic acid
no treatment
dark adsorption
0.5 min
1.0 min
5.0 min
10.0 min

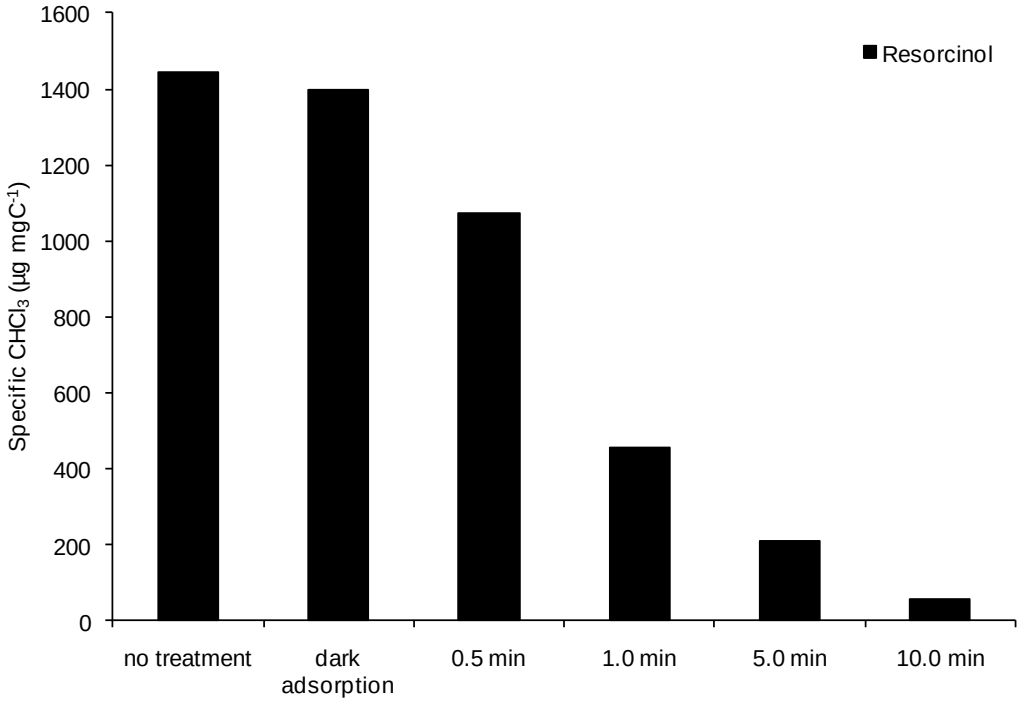
5.2 (D)


Specific $CHCl_3FP$ (µg $mgC^{-1}$)
60
50
40
30
20
10
0
Glutamic acid
Aspartic acid
Glycine
Leucine
Serine
0 7 0
5 4 0
3 4 0
0 3 0
2 2 0
2 1 3
No treatment
Dark adsorption
0.5 min
1.0 min
5.0 min
10.0 min

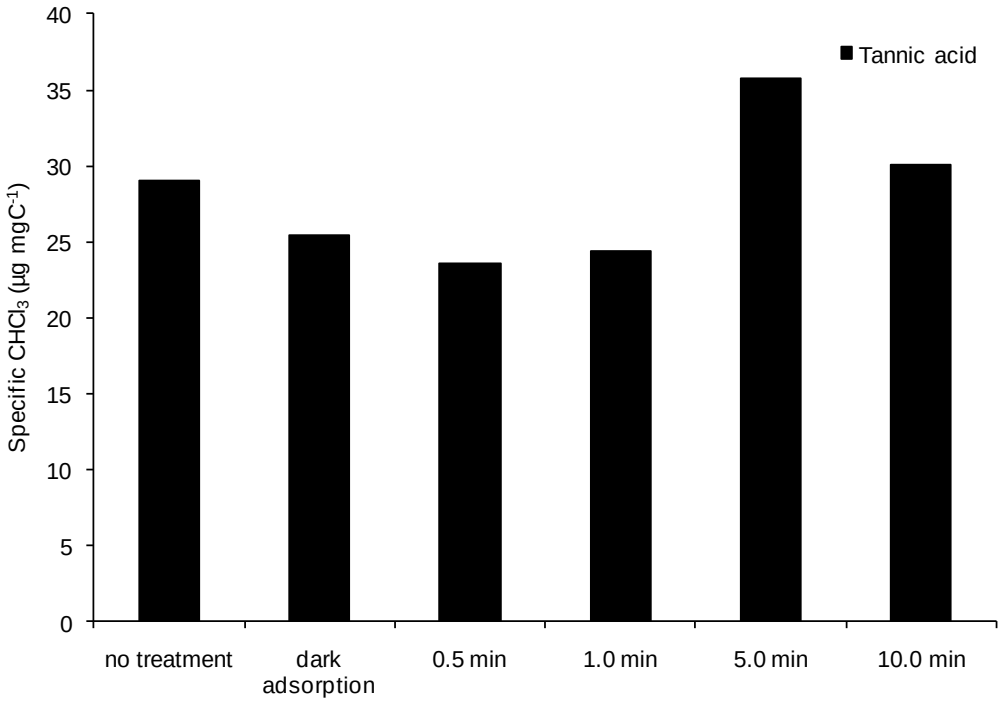
5.3 (A)


Specific $CHCl_3$ (µg $mgC^{-1}$)
16
14
12
10
8
6
4
2
0
Mannose
Xylose
No treatment
Dark adsorption
0.5 min
1.0 min
5.0 min
10.0 min

5.3 (B)


1600
1400
1200
1000
800
600
400
200
0
Specific $CHCl_3$ (µg $mgC^{-1}$)
Resorcinol
no treatment
dark adsorption
0.5 min
1.0 min
5.0 min
10.0 min

5.3 (C)


40
35
30
25
20
15
10
5
0
Specific $CHCl_3$ (µg $mgC^{-1}$)
Tannic acid
no treatment
dark adsorption
0.5 min
1.0 min
5.0 min
10.0 min

5.3 (D)

**Figure 5.3 Impact of photocatalytic oxidation on $CHCl_3FP$ (in µg $L^{-1}$) for amino acids (A), carbohydrates (B), resorcinol (C) and tannic acid (D) from 0 to 10 min retention time (1 g $L^{-1}$ as $TiO_2$ dose).**

**Figure 5.4 Impact of photocatalytic oxidation on the specific $CHCl_3FP$ (in µg $mg_{DOC}^{-1}$) for amino acids (A), carbohydrates (B), resorcinol (C) and tannic acid (D) from 0 to 10 min retention time (1 g $L^{-1}$ as $TiO_2$ dose).**

## 5.5 Conclusions

We have studied the photocatalytic oxidation of a range of NOM surrogates to investigate how the characteristics of NOM relate to treatability. The adsorption of compounds is normally controlled by their size, hydrophobicity and charge; here results revealed that large, hydrophobic and anionic tannic acid was the only compound significantly removed during dark adsorption onto $TiO_2$. The other two anionic species, $_L$-glutamic and $_L$-aspartic acid were moderately removed suggesting that even though both compounds are small and hydrophilic electrostatic interactions are likely to play a role during adsorption onto $TiO_2$. Photocatalytic oxidation showed significant potential for removing all the NOM surrogates tested and especially so for resorcinol , $_L$-glutamic acid, glycine and $_D$-xylose where residual DOC levels were below 1 mg $L^{-1}$ after 10 minutes of oxidation. For the remaining compounds the removals were still over 70% and greater than expected for conventional processes such as coagulation but no trend was identified between chemical character and removal. The

energy requirements to achieve this level of removal would need to be significantly reduced before this would be an economically viable process.

THM removal generally followed DOC removal although for $_{L}$-leucine photocatalytic oxidation significantly increased the $CHCl_3$FP indicating the formation of reactive by-products. This would be a concern for the application of photocatalytic oxidation for water treatment and there would be a need for downstream treatment processes such as GAC or biological treatment to remove these by-products before any disinfection stage.

## 5.6 References

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Bolto, B., Dixon, D., Eldridge, R. (2004) Ion exchange for the removal of natural organic matter. React Funct Polym **60**(1-3), 171-182.

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# 6 Implications for water utilities

## 6.1 Are high alkalinity hydrophilic rich surface waters treatable by AOPs?

One of the first points that water utilities should take into account when considering an AOP to remove NOM are the characteristics of the organics to be treated. Studies on real waters indicate that humic rich waters are more suitable for AOP treatment as they are composed of high MW hydrophobic compounds such as aromatics and double bonded systems which have been reported to be preferentially attacked by hydroxyls radicals (Chapter 2). This is supported by our findings as lower bulk removals were obtained after UV/$H_2O_2$ (Chapter 3) and photocatalytic oxidation (Chapter 4) treatment of a hydrophilic rich water in comparison with the humic rich waters described in the literature. Although direct comparison is not always possible due to different experimental conditions being used (Chapter 2). Interestingly, the UV/$H_2O_2$ treatment of a range of NOM surrogates to investigate hydroxyl radical reactivity suggests that there is no relationship between NOM physical properties such as hydrophobicity and removal (Bond *et al*., 2009). In a similar way, we have shown that there is no evidence of hydroxyl radical selectivity during the photocatalytic oxidation of the same range of NOM surrogates (Chapter 5). Overall, it is thought that hydroxyl radicals react preferentially but not selectively with high MW hydrophobic compounds. Therefore providing sufficient energy, all types of organics (hydrophobic and hydrophilic) would be degraded although

this would need to be confirmed experimentally using mixtures of model compounds with different properties. These findings imply that the application of AOP treatment at full scale would require significantly more energy for hydrophilic in comparison to hydrophobic rich waters in order to achieve satisfactory NOM removal and is likely to be uneconomic. The cost of conventional coagulation of a high alkalinity water (180 mg $L^{-1}$ as $CaCO_3$) was evaluated taking into account the pH adjustment (HCl and NaOH addition) as well as the coagulant dose (Table 6.1). The following values were assumed: £2.5 per Kg for ferric sulphate (coagulant); £6 per Kg for NaOH; £100 per MT (Mega Tonne) for HCl. Regarding the AOP cost, the electrical energy per order (£0.1 per kWh) and $H_2O_2$ or $TiO_2$ dose were considered (£2.25 per Kg for $TiO_2$; £16 per Litre for $H_2O_2$ at 30%). It is obvious that the high $E_{Eo}$ found in this study result in high cost and that further optimisation of the AOP process is needed as discussed in 6.2.

**Table 6.1 Comparison of operating costs associated with coagulation, UV/$H_2O_2$ and UV/$TiO_2$ processes**

| | **HCl** $gm^{-3}$ | **NaOH** $g\ m^{-3}$ | **Ferric sulphate** $g\ m^{-3}$ | **Electrical energy** $kWh\ m^{-3}$ | **$H_2O_2$** $g\ m^{-3}$ | **$TiO_2$** $g\ m^{-3}$ | **Cost** $£.m^{-3}$ | **Cost** $£.d^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| Coag. | 66 | 72 | 5 | - | - | - | 0.3 | 9300 |
| UV/$H_2O_2$ | - | - | - | 10 | 17 | - | 1.4 | 41100 |
| UV/$TiO_2$ | - | - | - | 500 | - | 1000 | 42 | 1260000 |

*Plant flow – 30000 $m^3.d^{-1}$*

In addition, water utilities should also take into account the composition of the water matrix before implementing an AOP at full scale. For example, the water alkalinity needs to be considered as carbonate species have been shown to

scavenge hydroxyl radicals and therefore be detrimental to NOM removal (Chapter 2). The presence of significant concentrations of hydroxyl radical scavengers in a water would result in increased energy and chemical costs in order to maintain the process performance.

The results of this investigation which dealt with real waters as well as model compounds highlight the fact that AOP efficiency is difficult to predict as it is linked to both the characteristics of the organics and to the water matrix. This implies that simple monitoring of a single physical property (such as charge using zeta potential measurement on site) would not be sufficient as a tool for selecting an appropriate AOP to treat a specific water. Water utilities should carefully consider the various physical properties of NOM (size, hydrophobicity, charge) as well as the water matrix composition which are both site specific before implementing an AOP in a drinking water treatment flowsheet.

Sarathy and Mohseni (2010) suggested that NOM low in MW, hydrophobicity and aromatic character would be mineralised after UV/$H_2O_2$ at typical commercial treatment doses (2 J $cm^{-2}$ and 15 mg $L^{-1}$ as $H_2O_2$). This was not observed in our study although the UV and $H_2O_2$ doses were higher. The high alkalinity of our water acting as hydroxyl radical scavenger is an obvious explanation of this difference. It should be noted that the apparent MW cannot be compared as this parameter was not precisely determined in our study (only the elution time was monitored and linked to MW range). Overall, this shows that the AOP treatment of high alkalinity waters has limited applications unless a softening pre-treatment is implemented upstream.

## 6.2 What are the current limitations of such processes?

Water utilities should also consider the formation of oxidation by-products before full scale implementation of an AOP, as previous investigations have shown that photochemical treatment rarely results in a complete mineralisation of the organics even at high UV doses (200 J $cm^{-2}$) (Chapter 2). This is supported by our findings which showed evidence of formation of low MW oxygenated by-products (Chapter 3 and 4). Further supporting data can be found in the literature, for example, the UV/$H_2O_2$ treatment of a raw surface water (2 mg $L^{-1}$ as DOC) using a UV dose of 1 J $cm^{-2}$ and 20 mg $L^{-1}$ $H_2O_2$ (0.6 mM) resulted in the formation of 100 µg $L^{-1}$ of formaldehyde (Sarathy and Mohseni, 2009). This highlights the need for water utilities to implement a downstream process to remove these by-products as they could present potential health concern and contribute to biofilm formation in the distribution system (Chapter 2-3). In addition, we demonstrate that short time UV/$H_2O_2$ and photocatalytic oxidation could lead to an increase in THMFP implying that treatment time should be optimised for the studied water before being applied on a larger scale considering that treatment time, reactor volume and UV intensity are interrelated (Chapter 3 and 5). To illustrate, UV/$H_2O_2$ treatment of the real water resulted in a THMFP increase from an initial value of 402 µg $L^{-1}$ to 672 µg $L^{-1}$ after 3 J $cm^{-2}$ and 1 mM initial $H_2O_2$ while it was reduced to 265 µg $L^{-1}$ after 6 J $cm^{-2}$ and 1 mM initial $H_2O_2$. Although few studies have investigated

the toxicity of AOP by-products and no cytotoxicity or mutugenicity has been reported to date (Chapter 2), it is recommended that this aspect is considered prior to an implementation of AOP in a drinking water flowsheet. It should be noted that preliminary Microtox® Acute Toxicity tests conducted on the same raw water, resorcinol and $_{L}$-glutamic acid treated by UV/$H_2O_2$ (6 J $cm^{-2}$ and 0.5 mM $H_2O_2$) were all negative (Bobion, 2009) but a more comprehensive set of tests should be carried out prior to conclusions being made.

Residual $H_2O_2$ after UV/$H_2O_2$ treatment should also be considered by water utilities as it is a cytotoxic bacterial mutagen and it also interferes with disinfection processes by reaction with chlorine. GAC has been shown to effectively remove residual $H_2O_2$ at full scale when 6 mg $L^{-1}$ was used as an initial concentration (Kruithof *et al*., 2007). This is supported by our study where no significant residual $H_2O_2$ was found at the effluent of the GAC columns using 17 mg $L^{-1}$ as $H_2O_2$ initial concentration.

The other key aspect that water utilities should take into account in the application of photochemical processes is the energy requirements of UV systems. This study has highlighted that efficient NOM treatment may require higher UV doses than typical doses applied for disinfection (2-4 J $cm^{-2}$) (Chapter 2). The electrical energy per order ($E_{Eo}$) is calculated using the electrical energy used by the irradiation system, the treated volume, the duration of treatment and the ratio of initial pollutant concentration (DOC here) by final pollutant concentration (Bolton and Stefan, 2002). In the UV/$H_2O_2$ study $E_{Eo}$ values ranged from 5 to 15 kW h $m^{-3}$ while an $E_{Eo}$ of 0.54 kW h $m^{-3}$

achieved 80% atrazine removal at full scale using an optimised reactor (Kruithof *et al*., 2007). This highlights the importance for water utilities to fully optimise their reactor design to lower the energy costs. $E_{Eo}$ for the photocatalytic oxidation reactor varied between ~600-2000 kW h $m^{-3}$. It is worth noting that energy loss by heat transfer which was substantial in the reactor is not taken into account in the $E_{Eo}$ calculation. Photon scattering should also be considered as about 70% of the emitted photons are scattered while 30% are adsorbed (Li Puma *et al*., 2004; Colina-Marquez *et al*., 2010). However the results of this study have clearly shown that the UV dose has a significant impact on the process performance. Ongoing research in photocatalytic oxidation could provide alternative UV sources such as UV light emitting diode (UV LED) radiation with controlled periodic illumination which could be more effective and durable (Wang and Ku, 2006; Chen *et al*., 2007).

When opting for photocatalytic oxidation using $TiO_2$ nanoparticles slurry, water utilities would need to consider an additional process for separation of the $TiO_2$ particles from the treated water. Photo-Cat Lab® from Purifics® (Gerrity *et al*., 2009) and MC-R® from WaterInnovate® (Pidou *et al*., 2009) offer the potential of obtaining $TiO_2$ free effluent by coupling the UV/$TiO_2$ process with a membrane filtration.

It should be noted that UV technology can be applied in various areas such as criminology (Detection of Altered Documents), electronics (Clean Room Inspection), archaeology, automotive (Leak Detection), medical (Phototherapy).

Point of use UV purifiers can also be used in private water supplies or whole houses.

## 6.3 Can NOM removal be enhanced by an AOP pretreatment followed by a downstream process?

A first option for water utilities to consider is the implementation of an AOP as a pretreatment to coagulation. However, the findings of this investigation concerning UV/$H_2O_2$ have shown no significant benefits of this combination as UV/$H_2O_2$ and coagulation appeared to target the same compounds (high MW, hydrophobic). This study confirmed that treatability by the coagulation is determined by the physical properties of the organics such as size, hydrophobicity and charge (Chapter 3).

The second option for water utilities is to implement an AOP followed by a downstream process such as fresh GAC or biotreatment. Columns test (RSSCT) results showed that photocatalytic oxidation combined with fresh GAC increased significantly both NPOC and THMFP removals compared with GAC alone (Chapter 4). In the case of UV/$H_2O_2$, the benefits were more limited (Chapter 3). These differences in performance between the two AOPs coupled with GAC could be explained by the fact that the UV systems and water quality differed for both set of experiments. As in the case of coagulation, this study confirms that NOM characteristics such as size and hydrophobicity were the key properties influencing the treatability by GAC.

Biodegradation processes are likely to be dominant in GAC adsorbers after extended treatment period so water utilities should consider the biodegradability of the water to be treated. The results of the bench scale study presented here revealed limited benefits of both UV/$H_2O_2$ and photocatalytic oxidation coupled with biotreatment but column tests should be conducted to confirm this trend. The literature indicates that substantial UV doses (10-26 J $cm^{-2}$) are required to achieve significant increase in BDOC which would be uneconomic (Chapter 2). Another implication for water utilities is that AOP/biotreatment could only be applied to raw waters amenable to biodegradation, for example algal organic matter (AOM) influenced sources. Waters containing significant amounts of non adsorbable DOC would be refractory to biotreatment (Chapter 2).

Another option would be to implement an AOP as a polishing process before the chlorination step. However, we have shown that AOP treatment of NOM resulted in the formation of potentially toxic oxygenated by-products. THM precursors were also formed after AOP treatment. A downstream process such as GAC or biological treatment is therefore necessary to remove those by-products.

## 6.4 References

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# 7 Conclusions and future work

## 7.1 Conclusions

- The literature review highlighted the fact that humic rich waters composed of high MW, hydrophobic compounds were easier to treat by UV/$H_2O_2$ and photocatalytic oxidation than low MW, hydrophilic compounds. The water matrix was found to affect the process efficiency as ionic species such as carbonates scavenge hydroxyl radicals. Complete mineralisation was rarely reported even at high UV doses (> 200 J $cm^{-2}$). Most studies involving an oxidation process coupled with a downstream process involved ozonation. The combination of ozonation with coagulation showed contradictory effects on NOM removal which mainly depended on the ozone dose. Adsorption of organics onto fresh GAC was both affected by size and surface chemistry. Most studies reported no significant benefit of ozonation pretreatment onto fresh GAC adsorption. On the other hand, biodegradability was substantially enhanced after treatment highlighting the potential of downstream BAC.

- The investigation of UV/$H_2O_2$ treatment on a high alkalinity hydrophilic rich water revealed moderate NPOC removal at UV doses up to 6 J $cm^{-2}$ and 2 mM of initial $H_2O_2$. However significant structural changes of the organics were observed: loss of aromaticity and double bonded character, shift towards lower MW more hydrophilic compounds and

formation of oxygenated by-products such as carboxylic acids, ketones/quinones. As a consequence the reactivity to chlorine was enhanced significantly at doses ≤ 3 J $cm^{-2}$ and reduced at 6 J $cm^{-2}$ indicating that THM precursors were further degraded.

- Combining UV/$H_2O_2$ with coagulation did not show any significant benefits when compared to coagulation alone which is not unexpected given that oxidation lead to a decrease in the charge and hydrophobicity of the organics produced. UV/$H_2O_2$ appeared to target similar components as coagulation. Batch tests using fresh GAC revealed that coagulated-UV/$H_2O_2$ treated water had a lower adsorption capacity than untreated water while dynamic columns tests revealed moderate benefits of the same combinations of processes showing that the UV dose used was a key parameter to THM precursor removal. The combination with biotreatment in batch did not exhibit any significant benefits in terms of NPOC and THMFP removal as the UV doses applied are thought to be too low to affect significantly the biodegradability while a portion of NOM is believed to be refractory to biodegradation.

- The photocatalytic oxidation of a high alkalinity hydrophilic rich water showed significant NPOC and $UV_{254}$ removal at 0.5-10 min retention time (MP lamp, 630 W) and 1 g $L^{-1}$ as $TiO_2$ dose. Loss of aromaticity and double bonded character, shift towards lower MW more hydrophilic compounds were observed although complete mineralisation was not achieved. The THMFP (in µg $L^{-1}$) was reduced after treatment although

the reactivity to chlorine (in µg $mgC^{-1}$) of the oxidation by-products remained unchanged.

- The GAC batch tests showed that adsorption capacity of the UV/$TiO_2$ treated water was reduced compared with raw water due to an increase in hydrophilicity and hence solubility of the organics. On the contrary, the GAC columns tests (RSSCT) showed a beneficial impact of photocatalytic pretreatment on GAC adsorption both in terms on NPOC and THMFP uptake. This was explained by the fact that the organics were broken down into smaller molecules that could diffuse more easily into the internal pore structure of the activated carbon. Overall, it appeared that surface chemistry (hydrophobicity) had a significant impact in the GAC batch tests while size was controlling the adsorption in the GAC dynamic columns tests. Photocatalytic oxidation had a limited effect on the biodegradability of the studied water and UV/$TiO_2$ coupled with biotreatment did not enhance significantly NOM removal.

- Investigation using nine NOM surrogates (five amino acids, two carbohydrates, two phenolic compounds) demonstrated that $TiO_2$ dark adsorption preferentially removed large, hydrophobic and anionic tannic acid highlighting that size, hydrophobicity and charge were key parameters influencing the adsorption onto $TiO_2$. Significant DOC and THMFP removals were observed for all compounds after photocatalytic oxidation except for $_L$-leucine where an increase in chlorine reactivity was observed. However no relationship was found between NOM physical

properties and removal. The high energy levels used in this study suggest the need of optimising the process so that it become economically viable.

## 7.2 Future work

- Further investigation by GC/MS or GC/FT-IR should aim at determining the composition of the NOM in raw water as well as the oxidation by-products formed including non regulated DBPs and oxygenated compounds (aldehydes, ketones, carboxylic acids). It would be interesting to compare the nature and the amount of by-products formed after UV/$H_2O_2$ and photocatalytic oxidation to have a better understanding of the mechanisms occurring within the same treatment conditions.

- More research should focus on each individual fraction of the water and its treatability by the different process combinations to further understand the role and reactivity of each fraction of the reservoir water.

- A comprehensive toxicity and mutagenicity assessment is recommended before AOP application at full scale to ensure health concerns are insignificant.

- The reactivity of hydroxyl radicals has been tested with individual NOM surrogates and complementary work should involve mixtures of

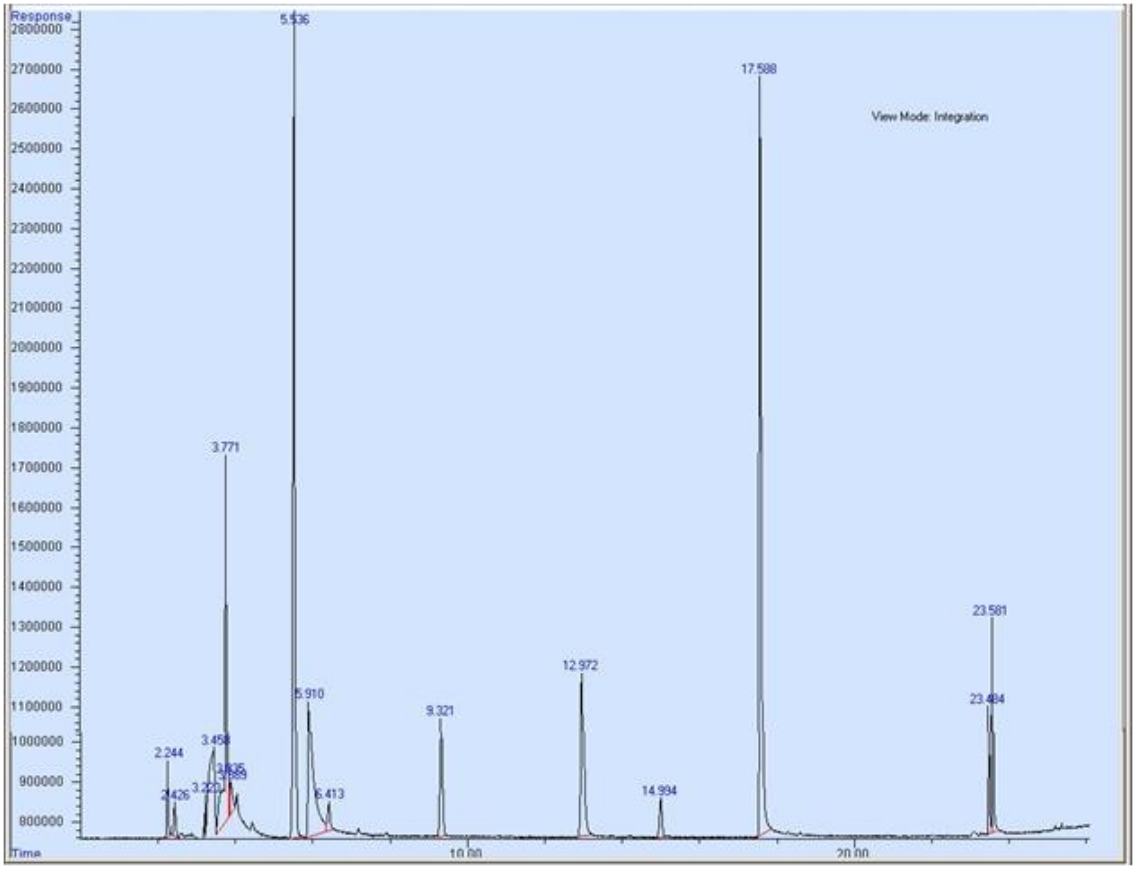
compounds to further investigate the reaction mechanisms between model compounds and hydroxyl radicals and other reactive species.

- Our study highlighted the great potential of AOPs although energy requirements would be currently uneconomic to be implemented at full scale by water utilities. Therefore further research should aim at optimising the UV reactor performances (design, configuration, UV lamp). The use of models also allow accurate calibration of the UV reactors.

- Further study is recommended on the combination of GAC and $H_2O_2$ as formation of hydroxyl radicals has been reported which could further degrade the NOM.

- Further work should investigate an alternative treatment to AOPs for the studied water. For example, a nanofiltration (NF) process using a hydrophobic membrane has been shown to remove efficiently small hydrophilic precursors such as amino acids and carbohydrates.

# 8 Annexes

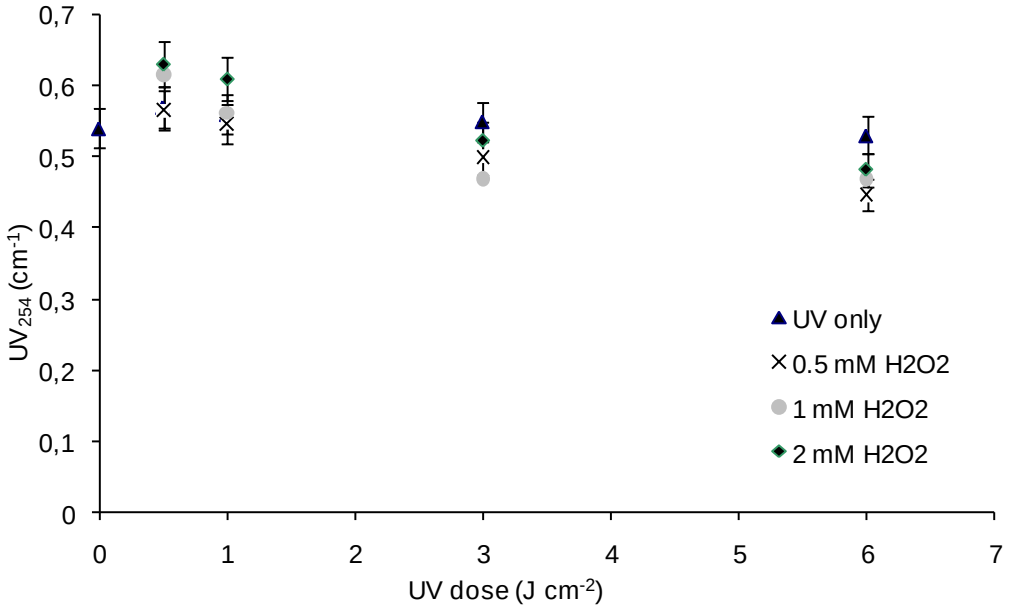



**GC ECD chromatogram for $THM_4$**

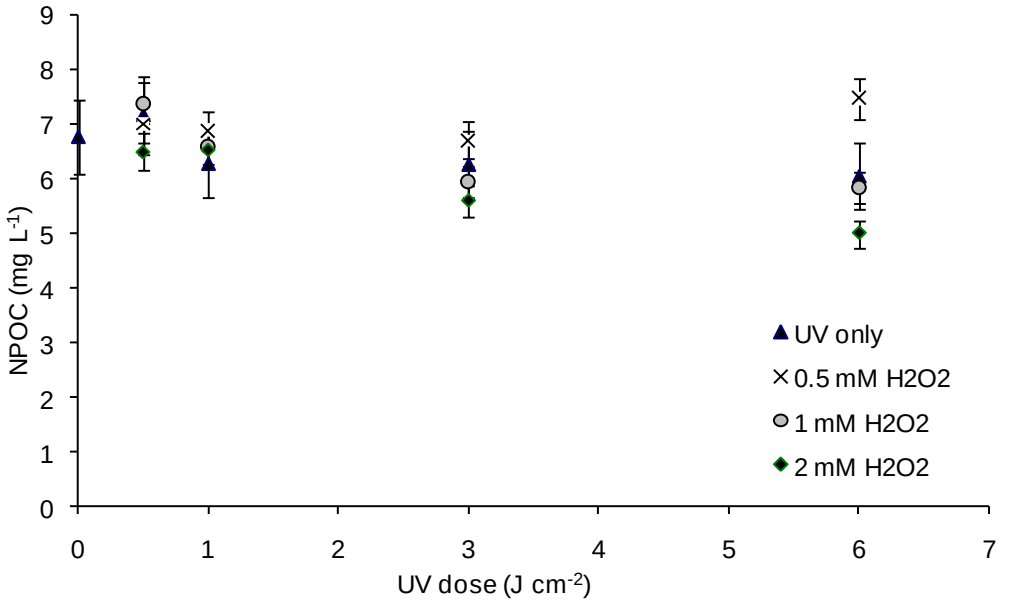
## Method performance

| Compound | Retention Time (min) | Relative Standard Deviation (%) | Detection limit (µg $L^{-1}$) | Minimum Reporting Level (µg $L^{-1}$) |
|---|---|---|---|---|
| $CHCl_3$ | 3.61 | 0.058 | 0.028 | 0.084 |
| $CHCl_2Br$ | 5.18 | 0.063 | 0.036 | 0.108 |
| $CHBr_2Cl$ | 8.68 | 0.045 | 0.049 | 0.148 |
| $CHBr_3$ | 14.36 | 0.037 | 0.095 | 0.284 |

(A)

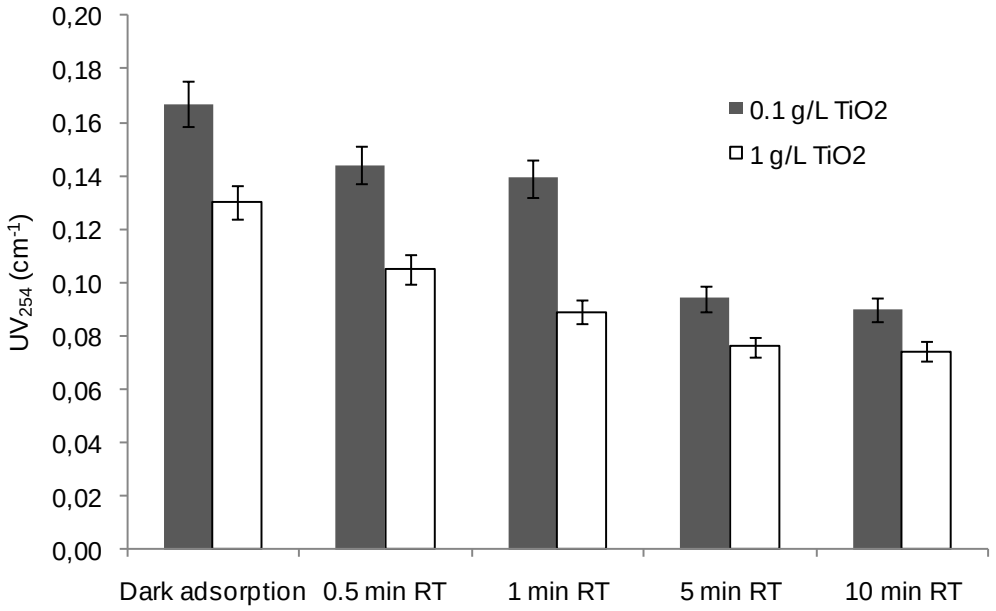



(B)

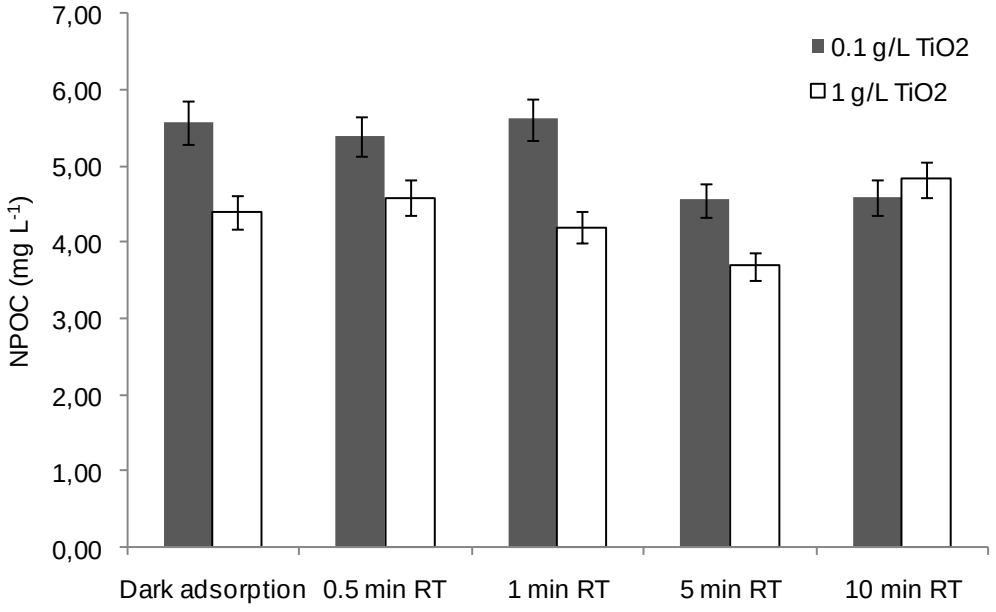



$UV_{254}$ (A) and NPOC (B) removals after UV direct photolysis and UV/$H_2O_2$ (0.5-2 mM as $H_2O_2$ initial concentration)

(C)




(D)




$UV_{254}$ (C) and NPOC (D) removals after $TiO_2$ photocatalysis from 0 to 10 min retention time (0.1-1 $TiO_2$ doses)